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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1638

Part of Journal of Research of the National Bureau of Standards, Volume 34, March 1945

COPPER REDUCTION OF DEXTROSE, LEVULOSE, INVERT SUGAR, AND SUCROSE-INVERT-SUGAR MIXTURES IN CITRATE-CARBONATE SOLUTION

By Richard F. Jackson* and Emma J. McDonald

ABSTRACT

The copper reduction values for dextrose, levulose, invert sugar, alone and in the presence of sucrose, have been determined, employing a modified Benedict's copper citrate-carbonate reagent and the iodometric titration method of Shaffer and Hartmann. It has been found that under carefully controlled conditions this method is inferior with respect to precision to the methods of Munson and Walker and of Lane and Eynon, in which caustic alkali is a constituent of the copper reagent. Because of its convenience, it is valuable for rapid work where a precision not greater than 0.5 percent is required.

A table of equivalents for use in routine sugar analysis has been computed.

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I. INTRODUCTION

Complex copper solutions in which the alkalinity is furnished by alkali carbonates and bicarbonates were proposed during an early period of reducing-sugar analysis, but such solutions have in general proved less reliable with respect to the reproducibility of analytical results than those containing caustic alkali. It has been shown[1] that

*Deceased.

[1] R. F. Jackson and E. J. McDonald, J. Assn. Official Agr. Chem. 24, 767 (1941).

independent operators using Munson and Walker's method for the analysis of pure sugars can attain a precision of about 0.2 percent within the range of 70 to 210 mg of reducing sugar. Lane and Eynon's method[2] has been found to compare well with Munson and Walker's method. Here the skill of the operator is a very important factor in determining the precision of the method. The authors say that titrations on a given sugar solution will agree well within 0.1 ml. Since their tables include values for a titration of 15 to 50 ml, the careful operator, using 25 to 50 ml for a titration should obtain a precision well within 0.4 percent. In spite of this fact, carbonate solutions have been widely advocated for reducing-sugar analysis because the mildly alkaline solutions attack accompanying "nonreducing" substances less than those containing caustic alkali. The carbonate-bicarbonate solutions have proved particularly serviceable for the determination of small quantities of reducing sugar in the presence of large percentages of sucrose. When caustic alkaline copper solutions are used for analyzing such mixtures, the reducing power of sucrose is relatively large and uncertain. Such analyses are of special importance in European countries, where great significance is attached to the reducing-sugar content of raw beet sugar, and consequently a number of methods have been recently elaborated in which, invariably, mildly alkaline copper solutions have been employed.[3] In this country, however, where a somewhat wider variety of sugar products is encountered, the requirements for a reducing-sugar method are more general and a satisfactory method should be applicable to the entire range of ratios of sucrose to reducing sugar.

In modern reducing-sugar analysis the tendency has been to determine the reduced or unreduced copper in the original reaction vessel by iodometric titration, a procedure which is particularly well adapted to the carbonate methods. Thus convenience and rapidity are added to the other advantages. There remains, however, the fact that the carbonate methods have yielded less reproducible results than the caustic alkali methods. In the present investigation an effort has been made to determine the cause of some of these uncertainties and to ascertain the precision that is attainable under carefully controlled conditions. Since the method selected was rapid and convenient, it was found feasible to conduct a considerable number of analyses and to include a wide range of concentrations of sugars and sugar mixtures.

II. PRELIMINARY EXPERIMENTS

Preliminary to the extended series of measurements described in later paragraphs, a cursory study was made of various complex copper carbonate solutions, and measurements were made of the ratio of reduced copper to the dextrose taken for analysis. Quisumbing and Thomas,[4] in comparing the influence of different alkalies in alkaline copper solutions, found that the copper reduced by dextrose varied rapidly with change in carbonate concentration. It was also observed in this work that large variations in the ratio occurred with change of

[2] J. H. Lane and L. Eynon, J. Soc. Chem. Ind. **42**, 32T, 143T, 463T (1923).
[3] O. Spengler, F. Tödt, and M. Scheuer, Z. Wirtschaftsgruppe Zucker-Ind., **86**, 323 (1936); R. Ofner, Z. Zuckerind. Czechoslov. Rep. **58**, 36 (1933); N. Schoorl, Chem. Weekblad, No. 9 (1929); R. F. Jackson and E. J. McDonald, J. Assn. Official Agri. Chem. **26**, 462 (1943).
[4] F. A Quisumbing and A. W. Thomas, J. Am. Chem. Soc. **43**, 1510 (1921).

composition of the copper solution, amounting in extreme cases to about 50 percent. A partial compilation of such data is given in table 1. Evidently any change in composition of the copper reagent produces a relatively large change in the ratio of reduced copper to sugar taken. Many authors have used as a basis of selection those methods which yield the larger ratios of copper to sugar. It appears that the higher ratios of copper are not necessarily advantageous. The actual determination of copper is the most precise step in the whole analysis and the error of determination is not measurably diminished by having a slightly increased amount of it. Far more important considerations are the stability of the copper solution, the reproducibility of the analyses, and the smaller variations of the ratios with changing concentration of sugar. These advantages appeared to be combined in greatest degree in the copper citrate–carbonate reagents proposed by Benedict[5] and modified by Shaffer and Hartmann.[6] The latter authors, in a thorough investigation, determined by studying the respective equilibria, the exact conditions required for the quantitative iodometric titration of either cupric or cuprous copper. They found that the reaction

$$2\,Cu^{++} + 2\,I^- \rightleftarrows 2\,Cu^{+} + I_2$$

goes quantitatively to the left if the final concentration of copper and of iodide does not exceed 5 millimolar each. Since the cupric ions may be removed by the addition of potassium oxalate, they were able to determine cuprous copper in the presence of cupric copper at higher concentrations. As a result of this study, they proposed a procedure whereby an iodide-iodate solution is added to the cold reaction mixture and the reduced copper determined by thiosulfate titration.

TABLE 1.—*Effect of varying composition of copper reagent on ratio of reduced copper to dextrose*

Composition of copper reagent per liter		Ratio: mg of copper / 100 mg of dextrose	$\frac{\Delta R}{\Delta S}$[1]
$CuSO_4 \cdot 5H_2O$	Alkali salts		
Grams			
17.5	250 K_2CO_3, 100 $KHCO_3$	3.15	−0.0033
25	150 $KNaC_4H_4O_6.4H_2O$, 53 Na_2CO_3, 25 $Na_2HPO_4.12H_2O$.	2.653	−.0056
25	75 $KNaC_4H_4O_6.4H_2O$, 27 Na_2CO_3, 13 $NaHCO_3$.	2.572	−.0046
25	81 $K_2C_6H_6O_7.H_2O$, 70 K_2CO_3, 92 $K_2C_2O_4.H_2O$, 3.57 KIO_3, 50 KI.	2.197	−.0009
25	89 $Na_2C_6H_6O_7.2H_2O$, 53 Na_2CO_3	2.084	−.0010

[1] The mean change in the ratio caused by 1-mg increase in concentration of sugar between about 40 and 120 mg of dextrose.

In a limited number of experiments Shaffer and Hartmann showed that this method of copper analysis could be applied to copper reductions carried out in caustic alkaline solution or in citrate-carbonate solution. However, they confined themselves to an exhaustive study of a micromethod for determining dextroxe by means of a copper citrate–carbonate solution.

[5] S. R. Benedict, J. Biol. Chem. 5, 485 (1908).
[6] P. A. Shaffer and A. F. Hartmann, J. Biol. Chem. 45, 375 (1921).

As a macromethod, which is the subject of the present investigation, Shaffer and Hartmann suggested a modification of Benedict's solution containing potassium citrate, potassium carbonate, and copper sulfate. For convenience, they added potassium iodate, potassium iodide, and potassium oxalate, thereby combining in a single reagent all the chemicals required for the analysis up to the point of acidification and titration. As an alternative and mainly for the purpose of diminishing the cost of the chemicals, they described a similar solution containing sodium citrate and sodium carbonate. In this case it was necessary to prepare separate solutions of iodide-iodate and of potassium oxalate, since the latter would have caused the precipitation of sodium oxalate if added to the copper reagent.

1. EFFECT OF VARYING CITRATE CONCENTRATION

The precision with which the alkaline copper reagent must be prepared was first determined. Both sodium and potassium citrates contain water of crystallization which might conceivably be variable and hence render variable the concentration of dry substance. For reasons which are explained in a later paragraph, the sodium salts have been selected for preparing the reagents.

Trisodium citrate crystallizes with 5½ moles of water, which is theoretically 27.74 percent of the substance. On exposure of a pulverized sample to the air, it was found to lose more than 10 percent of this moisture overnight and more than 30 percent during a period of 3 days. On long standing, it approached a state corresponding to 2 moles of water. This same crystalline phase is reached by drying at 100° C for about 36 hours. With this tendency to effloresce, it was anticipated that the substance purchased from the supply houses might vary in water content. A sample of crystals from a freshly opened bottle contained 22.81 percent of moisture instead of the 27.74 percent required by theory. Other samples approached the theoretical water content more closely, although in variable degree.

Three alkaline copper reagents were prepared, each containing 25 g of copper sulfate crystals and 53 g of anhydrous sodium carbonate in 1 liter. One solution contained 71.435 g (0.20 mole) of trisodium citrate crystals, the second 89.294 g (0.25 mole), and the third 107.153 g (0.30 mole). Each of these solutions was used for the analysis of three 50-ml solutions of dextrose containing, respectively, 140.1, 113.5, and 56.3 mg of sugar, the copper being determined after a 5-minute period of boiling by the procedure described in detail. The results plotted in figure 1 are expressed as the ratio of reduced copper to the weight of sugar. It is at once evident that variations in the concentration of citrate exert a considerable effect and that as the concentration increases the amount of reduced copper diminishes. The differences in each series caused by a change of 0.05 mole (=18 g) in citrate concentration leads to the conclusion that in average such a change causes a difference of 0.04, or about 2 percent of the ratio. Since a precision of 0.1 percent is desired, the citrate concentration must be adjusted within about 0.9 g, that is $(0.002/0.04)\times 18$, or for a weight of 89.3 g (0.25 moles) within 1 percent. It is therefore necessary not only to weigh with this precision but to determine the moisture content of the trisodium citrate crystals.

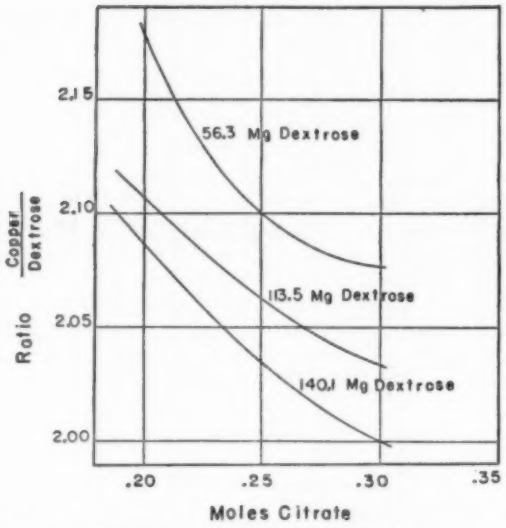

FIGURE 1.—*Variation in the copper-dextrose ratio with the amount of citrate present.*

To determine moisture in trisodium citrate, weigh rapidly a pulverized sample and dry at 100° C for 24 or 36 hours. Then dry to constant weight at 160° to 170° C, preferably allowing the temperature to rise gradually. The substance tends to decrepitate, and it is therefore advisable to cover the drying vessel loosely until the danger of loss is past.

2. EFFECT OF VARYING CARBONATE CONCENTRATION

Variations in the concentration of sodium carbonate also affect the ratio of reduced copper to sugar. Four alkaline copper reagents were prepared, in which the copper and citrate were held constant but in which the concentration of sodium carbonate was varied. With these solutions, analyses were made of 50-ml samples, each containing 100 mg of dextrose. As shown in figure 2, an increase in sodium carbonate concentration causes an increase in the ratio of reduced copper to sugar. Between 0.46 and 0.65 mole the ratio increases at the rate of 0.0443 for each 0.1 mole, or about 2 percent. For a precision of 0.1 percent, the variation in the ratio from this cause must not exceed 0.002, and therefore the concentration of carbonate must not vary more than $0.002/0.443=0.00475$ mole. If we arbitrarily select 0.5-mole concentration of sodium carbonate for the preparation of the copper reagent, its concentration must not vary by more than ± 0.00475 mole, or about 1 percent. Many samples of anhydrous sodium carbonate from the supply houses proved to be dry well within this tolerance, but others exceeded it slightly. Moisture can be very simply determined by heating a sample in a covered platinum crucible to dull redness, but care must be taken to avoid fusion of the salt. For the analyses described in the later paragraphs, the alkaline copper reagents were prepared with a precision well within the tolerances here indicated.

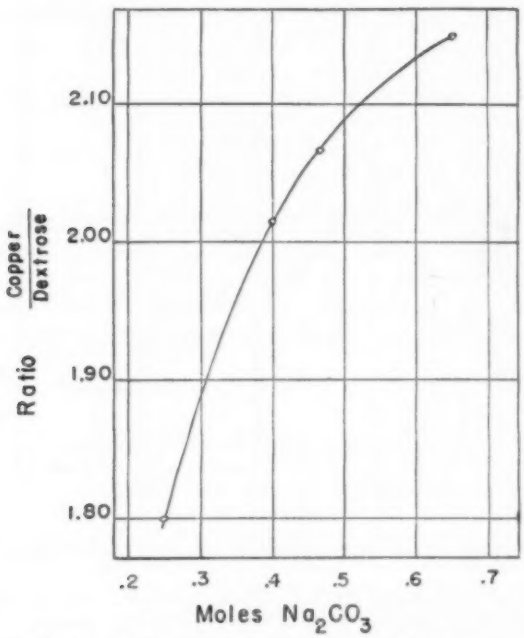

FIGURE 2.—*Variation in the copper-dextrose ratio with the amount of* Na_2CO_3 *present.*

3. RELATIVE MERITS OF SODIUM AND POTASSIUM SALTS FOR PREPARING REAGENTS

Both modifications of Shaffer and Hartmann's reagent were investigated. In one the copper reagent was prepared with tripotassium citrate, carbonate, and oxalate, and contained in 1 liter 3.57 g of KIO_3 and 50 g of KI. Fifty milliliters of the copper solution was pipetted accurately and the copper reduced by 50 ml of sugar solution. After the reduction was completed the reaction mixture was cooled and acidified with 20 ml of 5-*N* H_2SO_4.. The acidification caused the release of the equivalent of 50 ml of 0.1-*N* I_2, a part of which reoxidized the reduced copper, and the remainder was titrated back with standard thiosulfate. When the ratio of copper to sugar was plotted against sugar, the graph showed the same curvature as that with the sodium salts but with slightly different numerical values.

In the other modification the copper reagent was prepared with sodium salts. It was therefore necessary to prepare in separate solutions saturated potassium oxalate and the standard potassium iodide—potassium iodate solution. After extended experimentation with both of these modifications the latter was chosen and all of the later analyses were conducted with it alone. It appears at first glance that the convenience of combining all the chemicals in a single reagent has been sacrificed. However, the advantages of the second modification mentioned outweigh those of the combined reagent.

The combined reagent always contains the equivalent of 50 ml of 0.1-*N* I_2, regardless of the amount of copper reduced, and for the smaller concentrations of reducing sugar requires a long, tedious back titration. A blank determination must be run with great precision, since its value enters directly into all calculations. The thiosulfate must be standardized and its constancy assured by separate operations. On the other hand, when using the second modification in which the solutions of iodide-iodate and potassium oxalate are added just before titrating, one can gage roughly the quantity of the former to add in order to produce the slight excess necessary. Since potassium iodate can be obtained as a very pure chemical, the iodide-iodate can be prepared as a standard solution merely by weighing out the chemicals. Thus the working solution becomes the fundamental standard, and no additional standardization is required. If made slightly alkaline and if tightly stoppered, the solution keeps indefinitely.

4. IODIDE-IODATE SOLUTION

Shaffer and Hartmann proposed an iodide-iodate solution containing 5.4 g of KIO_3 and 60 g of KI in 1 liter. This solution upon acidification yields an equal volume of 0.1514-*N* I_2. In the present investigation 5.611 g of KIO_3 and 60 g of KI have been used. This solution upon acidification yields an equal volume of 0.1573-*N* I_2. This factor is the reciprocal times 10 of the atomic weight of copper, and 1 ml is exactly equivalent to 10 mg of copper. With the iodide-iodate solution adjusted to 0.1573 *N*, the calculation of reduced copper becomes very simple. The ratio of concentration of the standard iodate solution to that of 0.1-*N* thiosulfate is determined by titration of not less than 10 ml of the former. The back titration of thiosulfate in the analytical determination is then multiplied by this ratio factor and the thiosulfate thus converted to iodate. This is deducted from the measured volume of iodate added, yielding directly after multiplication by 10 the number of milligrams of copper reduced.

It is of course important that the KI shall be pure and free from iodate. Occasionally, potassium iodide becomes discolored after long standing, possibly indicating free iodine. Washing with chloroform, which restores its white color, and allowing it to dry in air purifies such samples. The iodide-iodate solutions were prepared at a known temperature, and when necessary, the measured volumes were corrected for variations of temperature by assuming an expansion coefficient of 0.0002.

5. EFFECT OF VARYING BOILING TIME

As is true of all reducing-sugar methods, the 5-minute boiling arbitrarily specified does not effect a maximum reduction of copper. It does, however, serve adequately for an arbitrarily selected terminal point. Figure 3 shows the rate of increase of precipitation of copper by 100 mg of dextrose for the several periods of boiling time. At the 5-minute point the ratio (2.195) is increasing at the rate of 0.01 per minute. Therefore, an error of 0.1 minute in judging the boiling time results in a difference of less than 1 part per thousand.

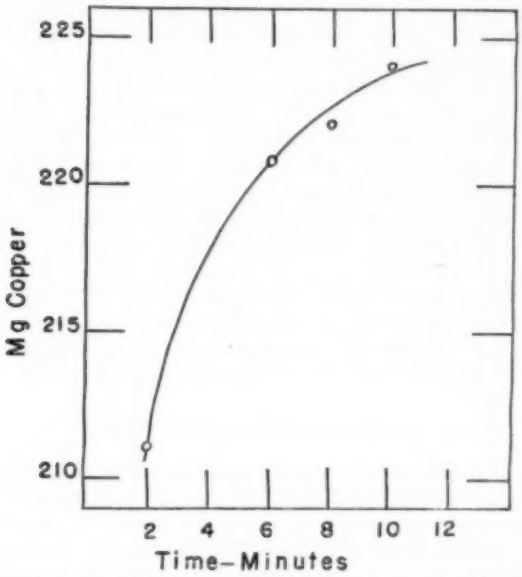

FIGURE 3.—*Effect of time of boiling on weight of copper reduced by 100 mg of dextrose.*

6. DETERMINATION OF BLANK

Blank determinations were made frequently by boiling the copper reagent with 50 ml of water. The mean value of copper found was 0.6 mg, with a mean deviation of 0.09 mg. Practically, this same value was found when the copper reagent itself was treated as in the analysis but without boiling. In other words, the value of the blank is not caused by autoreduction of the copper reagent, but is conceivably the result of a slight reduction of the copper by the iodine. This view is at variance with the findings of Shaffer and Hartmann, that the reaction given on page 215 runs quantitatively to the left in the presence of potassium oxalate of sufficient concentration, but, nevertheless, it was not possible to obtain the same titration values in the presence of copper and oxalate as in their absence.

These blank values are remarkably reproducible, and therefore all the data for reduced copper in the following tables have been left uncorrected for the blank. These uncorrected values are the more serviceable, since the analyst who makes only occasional analyses seldom makes a blank determination. If he does make a blank determination and finds a value different from 0.6 mg, he has merely to apply the difference as a correction.

III. DETAILS OF METHOD

1. REAGENTS

(a) *Modified Benedict's solution.*—Dissolve the equivalent of 64.52 g of anhydrous trisodium citrate or 89.29 g of crystals containing 5½ moles of water, the moisture content of which has been corrected for, and 53 g of anhydrous sodium carbonate in about 600 ml of water.

Add with vigorous agitation a solution of 25 g of $CuSO_4.5H_2O$ in about 150 ml of H_2O. Both solutions must be cool before mixing. Make to 1 liter and filter.

(b) *Standard potassium iodate solution.*—Dissolve 5.611 g of pure KIO_3 and 60 g of KI and make to 1 liter.

(c) *Saturated potassium oxalate solution.*

(d) *Sulfuric acid.*—Approximately 5 *N* (250 g of concentrated acid in 1 liter of solution).

(e) *Sodium thiosulfate.*—0.1 *N* (25 g of crystals in 1 liter).

2. PROCEDURE

Transfer 50 ml of solution (a) to a 300-ml Erlenmeyer flask and add 50 ml of a solution containing not more than 150 mg of reducing sugars. Mix with a rotary motion, cover the flask with a small inverted beaker, and place on a plate of asbestos gauze about 4.5 cm above the top of a gas burner.[7] Heat to boiling in 4 minutes and continue the boiling for exactly 5 minutes. In judging the beginning of the 5-minute period, disregard the early sporadic appearances of boiling and start the final period at the moment when the ebullition suddenly becomes violent. This occurs usually about 20 seconds after the first appearance of bubbles.

At the expiration of the prescribed period of boiling immerse without agitation in a cold-water bath, allowing to remain until cool. Add accurately a volume of standard iodate (b) in excess of that required for oxidation of the cuprous oxide and add approximately 20 ml of saturated potassium oxalate. Add by means of a rapidly delivering pipette 20 ml of 5-*N* H_2SO_4 and agitate with a rotary motion until the cuprous salts are completely dissolved. Examine the mixture by holding the flask above the level of the eye. Any undissolved cuprous oxide or cuprous sulfate can be clearly discerned and must be dissolved by continued agitation. Dilute to about 200 ml and add from a burette standard thiosulfate until the solution starts to turn from green to blue-green. Add starch indicator and complete the titration dropwise to the disappearance of deep-blue starch iodide, the final additions of thiosulfate being in split drops.

Determine the ratio of concentrations of thiosulfate to iodate, and by means of the factor thus obtained convert the thiosulfate volume to its equivalent volume of iodate. Deduct this from the volume of iodate added, and multiply the result by 10 to obtain the number of milligrams of copper reduced. From table 4 obtain the amount of reducing sugar corresponding to the weight of copper found.

IV. STANDARDIZATION

For the purpose of standardization, eight series of analyses were carried out. These included the reducing powers of pure dextrose, levulose, and invert sugar, and of sucrose–invert-sugar mixtures taken in such proportions that all possible ratios of the two were covered. The reducing sugar was varied from various low concentrations to about 150 mg in 50 ml. In each of the five series of analyses of sucrose–invert-sugar mixtures the sucrose was kept at a constant value and the invert sugar was varied.

[7] Electric heating may be used.

The sucrose and dextrose were National Bureau of Standards Samples 17 and 41, respectively. The sucrose was free from a measurable amount of moisture and the dextrose contained 0.01 percent of moisture, which was corrected for when the sample was weighed. The levulose was prepared by crystallization, once from water and three times from aqueous alcohol. When the crystals were dried for several hours at 60° C to constant weight, a small sample was found to suffer no further loss at 70° to 75° C. The levulose contained less than 0.002 percent of ash.

In preparation for analysis, a 500-ml solution was made up. This contained about 1.5 g of the sugar accurately weighed. Aliquot portions of this solution were taken by means of a series of odd-volume pipettes at roughly 2- to 5-ml intervals. These pipettes by frequent calibration were found capable of delivering the respective volumes of solution with a precision of 0.002 to 0.003 ml. The sucrose solutions were prepared of such concentration that 10 ml contained the weight of sugar desired. For the 10-g sucrose series the dry sugar was weighed directly into the reduction flask and 6 ml of water added to make a total calculated volume of 12.19 ml of solution. Invert-sugar solutions and water were added in such quantity that the total volume became 50 ml.

Invert sugar was prepared in the earlier measurements by inverting sucrose for 35 minutes at 70° C. in the presence of 0.1-*N* HCl. When cold the acid was neutralized with NaOH. Comparative measurements were made with invert-sugar solutions prepared by weighing equal quantities of dextrose and levulose. As no measurable difference was detected, the later measurements were made with the synthetic invert sugar solely.

When the Erlenmeyer flasks used for the reduction had dried in the air for several days the reaction mixtures boiled without bumping, but if the flasks were used more frequently, bumping occurred. The addition of talc in amounts of 2 mg or less prevented bumping and did not obscure the start of boiling.

1. EXPERIMENTAL RESULTS

The results of the reduction measurements made as described in previous pages are assembled in table 2. For each sugar a formula was devised to express the relation of sugar present to copper reduced. These formulas were prepared by the method of averages.

It is difficult to make an exact estimate of the precision of the method. The curves, figure 4, showing the relation of the copper-sugar ratio to copper, especially in the case of invert sugar, may shift an appreciable amount if the analysis is not carried out under exact conditions. Since the variations in gas pressure seemed to be sufficient to cause such a shift in the curves, a series of analyses was made over a period of time in which the heating was done electrically. The voltage of the current was stabilized by a voltage regulator and adjusted by a Variac. The flask was placed in a conical heater in such a way that the surface of the liquid was just below the top of the heater. Table 3 gives the results of this series of analyses.

TABLE 2.—*Milligrams of copper reduced by dextrose, levulose, invert sugar and sucrose—invert-sugar mixtures*

Sugar taken	Copper	Sugar by formula[1]	Error
	DEXTROSE		
mg	*mg*	*mg*	*mg*
145.5	295.9	145.1	−0.4
132.3	272.4	132.7	+.4
117.9	243.8	117.9	0
98.6	205.9	98.7	+.1
87.3	183.0	87.2	−.1
80.3	169.3	80.4	+.1
72.9	154.5	73.2	+.3
65.1	137.4	64.8	−.3
58.3	123.8	58.3	0
54.4	115.4	54.3	−.1
48.1	102.9	48.3	+.2
40.2	85.7	40.1	−.1
32.2	69.3	32.4	+.2
29.1	61.8	28.9	−.2
24.1	51.3	24.1	0
16.1	33.5	15.9	−.2
	LEVULOSE		
146.7	305.8	146.9	+.2
133.3	279.1	133.3	0
118.9	250.4	118.9	0
108.7	229.4	108.5	−.2
99.4	211.0	99.4	0
88.0	187.3	87.9	−.1
73.4	157.5	73.5	+.1
58.8	126.2	58.7	−.1
44.1	95.0	44.1	0
29.3	62.9	29.3	0
20.7	44.3	20.9	+.2
14.6	30.2	14.5	−.1
	INVERT SUGAR+10 g OF SUCROSE		
134.1	290.2	133.5	−.6
120.2	264.9	120.3	+.1
106.4	238.3	106.8	+.4
88.7	202.5	89.0	+.2
71.3	165.4	71.0	−.3
53.3	127.1	53.1	−.2
44.3	107.7	44.2	−.1
35.5	89.3	35.9	+.4
25.1	64.3	24.9	−.2
17.7	47.9	17.7	0

Sugar taken	Copper	Sugar by formula	Error
	INVERT SUGAR		
mg	*mg*	*mg*	*mg*
149.5	307.1	149.5	0
148.2	304.0	147.8	−0.3
141.0	290.6	140.9	−.1
140.2	289.4	140.2	0
135.8	280.8	135.8	0
134.7	279.2	135.0	+.3
127.4	264.8	127.5	+.1
120.1	250.7	120.4	+.3
113.6	238.1	114.0	−.4
100.4	210.8	100.3	−.1
95.0	199.9	94.8	−.2
84.6	179.7	84.9	+.3
74.8	159.3	74.9	+.1
74.2	157.8	74.4	+.2
59.4	126.4	59.3	−.1
56.5	120.8	56.6	+.1
56.2	119.7	56.1	−.1
59.9	127.4	59.8	−.1
44.9	95.8	44.8	−.1
42.4	90.5	42.4	0
37.4	79.4	37.2	−.2
44.5	95.1	44.5	0
42.1	89.8	42.0	−.1
35.0	74.6	35.0	0
29.6	63.1	29.6	0
19.8	42.0	20.0	+.2
14.0	28.9	14.1	+.1
	INVERT SUGAR +0.1 g OF SUCROSE		
148.4	306.6	149.0	+.6
140.8	290.1	140.4	−.4
133.0	275.7	133.0	0
117.7	245.3	117.5	−.2
98.3	207.4	98.4	+.1
78.8	167.6	78.8	0
59.0	126.5	59.0	0
49.1	105.4	49.0	−.1
39.3	84.6	39.3	0
27.7	59.6	27.7	0
11.8	24.6	11.8	0

Sugar taken	Copper	Sugar by formula	Error
	INVERT SUGAR +0.3 g OF SUCROSE		
mg	*mg*	*mg*	*mg*
148.4	306.4	148.1	−0.3
141.1	292.7	141.1	0
133.0	277.4	133.2	+.2
117.7	246.9	117.8	+.1
98.3	208.3	98.4	+.1
78.8	168.1	78.8	0
59.0	126.7	58.9	−.1
49.1	105.9	49.0	−.1
39.3	84.9	39.2	−.1
27.7	60.3	27.8	+.1
19.6	42.3	19.6	0
11.8	25.2	11.8	0
	INVERT SUGAR +1 g OF SUCROSE		
148.0	307.9	147.9	−.1
140.7	292.3	139.9	−.8
132.6	278.7	132.9	+.3
117.4	249.2	118.0	+.6
98.0	208.8	97.8	−.2
78.6	169.2	78.5	−.1
58.8	128.6	59.0	+.2
48.9	107.4	49.0	+.1
39.2	86.0	39.0	−.2
27.7	61.2	27.6	−.1
19.5	43.8	19.6	+.1
11.7	26.6	11.9	+.2
	INVERT SUGAR +3 g OF SUCROSE		
148.4	308.4	147.5	−.9
140.8	296.8	141.5	+.7
133.0	281.4	133.4	+.4
117.7	250.6	117.4	−.3
98.3	213.6	98.6	+.3
78.8	173.6	78.8	0
59.0	132.0	58.8	−.2
49.1	110.7	48.8	−.3
39.3	89.6	39.0	−.3
27.7	64.7	27.6	−.1
19.6	47.3	19.8	+.2
11.8	29.5	11.9	+.1

[1] Dextrose = 0.786 + 0.4476 Cu + 0.000135 Cu².
Levulose = 1.009 + 0.4432 Cu + 0.000110 Cu².
Invert sugar = 0.936 + 0.4435 Cu + 0.000131 Cu².
When 0.1 g of sucrose is present, invert sugar = 0.792 + 0.4442 Cu + 0.000128 Cu².
When 0.3 g of sucrose is present, invert sugar = 0.498 + 0.4457 Cu + 0.000118 Cu².
When 1 g of sucrose is present, invert sugar = −0.023 + 0.4438 Cu + 0.000119 Cu².
When 3 g of sucrose is present, invert sugar = −0.922 + 0.4308 Cu + 0.000165 Cu².
When 10 g of sucrose is present, invert sugar = −2.429 + 0.4117 Cu + 0.000195 Cu².

TABLE 3.—*Invert-sugar analyses*

Invert sugar taken	Invert sugar found in series—						Maximum error		Average error	
	1	2	3	4	5	6				
mg 140	*mg*	*mg*	*mg* 140.4 140.2	*mg* 139.7	*mg*	*mg* 139.6	*mg* 0.4	% 0.29	*mg* 0.32	% 0.23
120	119.8	120.1	120.1	120.4	120.0	119.9	.4	.33	.15	.12
100	99.9	100.1	100.5	100.0	100.4	99.8 99.9	.5	.50	.20	.20
80	79.9	80.0	80.3	80.2	80.2	79.9 80.0	.3	.38	.12	.15
60	59.7	60.0	60.2	59.9			.3	.50	.20	.33

The pure sugars, dextrose, levulose, and invert sugar, yield roughly parallel curves. As the concentration of sugar is diminished from 150 mg, the reducing powers pass through maxima in the vicinity of 40 mg of sugar or approximately 90 mg of copper, and then abruptly and very rapidly diminish, as shown in figure 4. The form of these curves is similar to that produced by levulose [6] in its reaction with Ost's solution at 55° C, the maximum reducing power in the latter case being at about 60 mg of levulose. The very rapid change of the ratios with concentration of sugar at the lower concentrations makes it questionable whether a satisfactory precision of analysis can be attained with these dilute solutions. For this reason, and because the number of experiments is insufficient to define these rapidly varying curves accurately, there is recorded in table 4 the milligrams of sugar corresponding to a minimum value of 100 mg of copper.

The precision of this method can be estimated by considering the deviation of analytical results from the calculated values. Of the 76 analyses falling within the range included in table 4, the number of analyses in which results deviate from the calculated values by specific amounts are as follows:

Number of analyses	Deviation
	Percent
3	0. 6 to 0. 5
7	0. 5 to 0. 4
15	0. 3 to 0. 2
22	0. 2 to 0. 1
22	0. 1 to 0

Ninety-six percent vary less than 0.5 percent, with 77 percent less than 0.3 percent.

The analyses of invert-sugar solutions given in table 3 are in agreement with these findings. When working with pure sugar solutions under carefully controlled conditions, the accuracy attained within the range given in table 4 agrees well with the precision of the method. If one is working with very dilute solutions or those in which more than about 300 mg of copper is reduced (the total amount of copper present is 318.2 mg), slight variations in the conditions may shift the curves given in figure 4 so that the results become less accurate, although duplicate analyses may agree well within the limits of the precision of the method. The precision of a reducing-sugar method in the analysis of products other than pure sugar solutions is so dependent upon the composition of the product that a general statement cannot be made. However, it can be said that in the analysis of five molasses samples investigated by this method, the end point could readily be determined and duplicate determinations agreed within 0.5 percent.

[6] R. F. Jackson and J. A. Mathews, J. Assn. Official Agr. Chem. 15, 204 (1932).

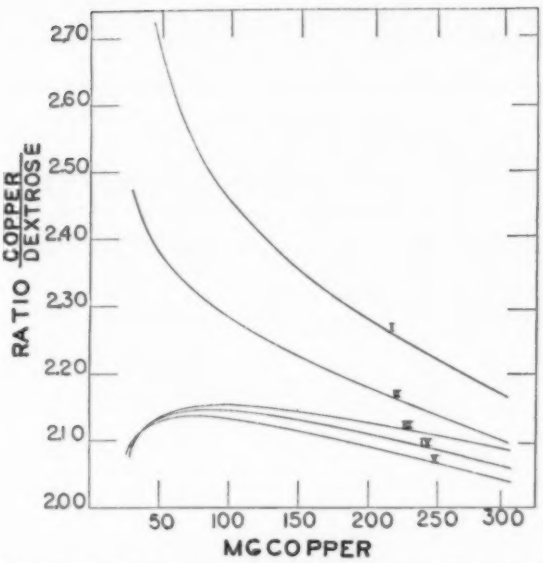

FIGURE 4.—*Change of the copper-sugar ratio with variation in the amounts of reduced copper.*

Curve I, Invert sugar+10 g of sucrose; II, invert sugar+3 g of sucrose; III, levulose; IV, invert sugar; V, dextrose.

It is interesting to note that quite in contrast to their relative reducing powers in the caustic alkali-copper reagents, levulose has in the copper carbonate solutions a greater reducing power than dextrose.

Sucrose alone has a reducing action, but the effect is much smaller in these copper carbonate solutions than in the caustic alkali-copper solutions. When analyzed alone pure sucrose solutions showed the following reducing powers, no corrections for blanks being applied:

Sucrose	Copper	Copper per gram of sucrose
g	*mg*	*mg*
10	10. 9	1. 09
8	10. 1	1. 26
6	8. 3	1. 38
4	6. 0	1. 5
2	4. 2	2. 1

When mixtures of sucrose and invert sugar are analyzed the reducing power of sucrose is apparently greater than when analyzed alone. At lower concentrations of invert sugar the reducing power of sucrose becomes an increasingly larger proportion of the total reducing power as the concentration of invert sugar is diminished.

TABLE 4.—*Table for calculating dextrose, levulose, invert sugar, and invert sugar in the presence of sucrose, (0.1 g, 0.3 g, 1.0 g, 3.0 g, and 10.0 g)*

Copper	Dextrose	Levulose	Invert sugar	Invert sugar				
				Plus 0.1 g of sucrose	Plus 0.3 g of sucrose	Plus 1.0 g of sucrose	Plus 3.0 g of sucrose	Plus 10.0 g of sucrose
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
100	46.9	46.4	46.6	46.5	46.2	45.5	43.8	40.7
110	51.7	51.1	51.3	51.2	51.0	50.2	48.5	45.2
120	56.4	55.8	56.0	55.9	55.7	54.9	53.2	49.8
130	61.3	60.5	60.8	60.7	60.4	59.7	57.9	54.4
140	66.1	65.2	65.6	65.5	65.2	64.4	62.6	59.0
150	71.0	70.0	70.4	70.3	70.0	69.2	67.4	63.7
160	75.9	74.7	75.2	75.1	74.8	74.0	72.2	68.4
170	80.8	79.5	80.1	80.0	79.7	78.9	77.1	73.2
180	85.7	84.4	85.0	84.9	84.6	83.7	82.0	78.0
190	90.7	89.2	89.9	89.8	89.4	88.6	86.9	82.8
200	95.7	94.1	94.9	94.8	94.4	93.5	91.8	87.7
210	100.4	98.9	99.8	99.7	99.3	98.4	96.8	92.6
220	105.8	103.8	104.8	104.7	104.3	103.4	101.8	97.6
230	110.9	108.8	109.9	109.7	109.2	108.4	106.9	102.6
240	116.0	113.7	114.9	114.8	114.3	113.4	112.0	107.6
250	121.1	118.7	120.0	119.8	119.3	118.4	117.1	112.7
260	126.3	123.7	125.1	124.9	124.4	123.4	122.2	117.8
270	131.5	128.7	130.2	130.1	129.4	128.5	127.4	123.0
280	136.7	133.7	135.4	135.2	134.5	133.6	132.6	128.2
290	141.9	138.8	140.6	140.4	139.7	138.7	137.9	133.4
300	147.2	143.9	145.8	145.6	144.8	143.9	143.2	138.7

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EFFECT OF AERATION ON HYDROGEN-ION CONCENTRATION OF SOILS IN RELATION TO IDENTIFICATION OF CORROSIVE SOILS

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ABSTRACT

Soils are generally air-dried to obtain comparable results in the measurement of pH. This paper points out the unreliability of such a procedure in measuring the pH of soils for the identification of corrosive areas. Large changes were observed in hydrogen-ion concentration of a poorly drained soil in passing from the moist field condition to the air-dried state and vice versa. This suggested a further investigation, and 62 air-dried soil samples taken from the National Bureau of Standards soil-corrosion test sites were saturated and stored without air for almost 1 year. Significant changes in pH were observed in the majority of the samples and large changes in many of them. It has been concluded that, for the identification of areas corrosive to iron and steel, pH measurements of soils should be made on samples maintained in the natural field condition.

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I. INTRODUCTION

In determining the pH values of air-dried samples of a soil a few months after the samples had been removed from the field, it was observed that the soil samples were very acid (pH 3.4 to 4.0). These measurements were in sharp contrast to the values obtained in the field, where determinations made on the soil in its natural state

showed a pH value of 7.2. Later, samples from the same location were collected and placed in tightly sealed jars and sent to the laboratory, where the pH determinations were found to be in full agreement with the measurements made in the field. The difference in the pH values of the soil in the fresh, moist condition and in the air-dried state suggested an investigation of the abnormal behavior of this soil.

II. PREVIOUS STUDIES ON pH VALUES OF SOILS AS AFFECTED BY AIR-DRYING

A number of soil investigators have studied the change in pH value of soil samples in passing from the fresh, moist field condition to the air-dried state. Some have reported that the only reliable measurements of pH are obtained in the field condition, whereas others have observed no appreciable change between the fresh and the air-dried samples.

Bailey [1] [1] made an extensive study of the effect of air-drying on 327 moist samples taken at different depths from 64 representative virgin profiles from widely scattered parts of the United States, Puerto Rico, and Canada. The fresh samples were placed in cans which were tightly sealed and sent to the laboratory where the hydrogen-ion measurements were made. The samples were then air-dried and the measurements repeated. Only 42 samples, or 13 percent of the total number examined, changed more than 0.1 pH unit. These 42 samples represented 20 soil profiles, or 31 percent of the profiles studied. Only 2 of the 64 profiles studied contained horizons or layers from which samples changed 0.50 pH unit or more. The maximum change in pH value was 0.68. Where the change on drying exceeded 0.1 pH, it was in the direction of greater acidity, with only two exceptions. Bailey concluded that hydrogen-ion determinations should be made on air-dried soils rather than on samples fresh from the field. This is in general agreement with Snyder [2], Healy and Karraker [3], Biilmann and Jensen [4], Arrhenius [5], Crowther [6], and Baver [7].

Results obtained by Snyder and by Healy and Karraker showed that air-drying of acid soils lowered the pH values slightly. Biilmann and Jensen studied 18 soils with a range of pH 5.2 to 8.3 and found that the air-dried soils were slightly more acid than the moist samples. They concluded that the air-dried samples had pH values which corresponded essentially to the values found before air-drying. Arrhenius reported the effect of drying on the hydrogen-ion concentration of one alkaline soil, finding that air-drying brought about no change. A comparison of fresh soils with air-dried samples by Crowther showed that the pH was generally reduced (about 0.1) by air-drying. The results obtained by Baver indicate that air-drying of acid surface soils does not significantly affect their pH values. However, air-drying of subsoils causes a marked increase in acidity which becomes greater with depth. He also observed a considerable decrease in alkalinity with alkaline soils. Both Crowther and Baver concluded that, for special purposes and detailed reaction studies, fresh, moist soils should be used in determining the pH, but for ordinary purposes the air-dried samples are sufficiently accurate.

[1] Figures in brackets indicate the literature references at the end of this paper.

Further information concerning the influence of air-drying soils was also obtained by Burgess [8], McGeorge [9], and Rost and Fieger [10]. Burgess found that drying had little effect on the hydrogen-ion concentration of acid soils. However, the drying of alkaline soils rendered them decidedly less alkaline. McGeorge observed that the pH values of alkaline calcareous soils were increased slightly by drying the soil in air. The results of Rost and Fieger showed a general tendency for air-dried soils to become more acid than the fresh ones. The acid samples showed as great a change upon air-drying as did the alkaline ones. They concluded that the only reliable indication of conditions existing in the field is obtained when hydrogen-ion determinations are made on soil samples in their natural state.

The effect of moistening and storage upon the hydrogen-ion concentration of samples of soil which had been air-dried was studied by Rost and Fieger [10]. Air-dried samples were remoistened with distilled water and stored in air-tight containers. Hydrogen-ion concentrations were determined at intervals up to 60 days. These investigators concluded that the air-dried samples had hydrogen-ion concentrations no more nearly reliable than the previously dried soils which were remoistened and stored with the exclusion of air.

The season of the year in which the soil sample is taken is of importance in the case of some soils. Periodic fluctuations have been observed in the pH values of soils by Baver [7], who found that the acid soils studied showed a continuous increase in hydrogen-ion concentration from May to September (0.92 pH maximum variation) and a return to approximately the same value each spring. He also found that the alkaline soils showed no consistent variation during the same period. Results obtained by Kelley [11] from monthly tests over a period of a year showed variations in pH values that amounted to as much as 1.0 pH in both surface soil and subsoil. Lipman and coworkers [12] found fluctuations of about 0.7 pH in surface soils between May and November.

From the results of the above-mentioned investigators who studied many different soil types, it is evident why soil samples are generally dried in air in order to obtain comparable results in pH measurements. In most of the cases the change in the pH between the fresh sample and the air-dried soil was less than 0.1 unit. A number of the samples changed by as much as several tenths of a pH unit, and only in a few cases did the variation approach or exceed one pH unit.

III. EFFECT OF AERATION ON THE HYDROGEN-ION CONCENTRATION OF AN ANAEROBIC SOIL

1. DESCRIPTION OF SOIL AND TEST LOCATION

The soil samples on which the studies were made were obtained from one of the sites at which corrosion tests are being conducted by the National Bureau of Standards. The site is located in Portage County, Ohio. A section of a pipe line on which severe corrosion caused by the activity of sulfate-reducing bacteria has occurred traverses this test site. The soil was classified as Papakating silty clay loam. The samples were taken at a point where the water table is at the surface of the soil throughout the year; hence, the soil

is completely saturated at all times, drainage and aeration being very poor.

The Papakating soils belong to a series of soils which have developed in first bottom lands. They have been deposited by the present streams and are the wash from the surrounding uplands, where the bedrock consists primarily of sandstone and shale. As the Papakating series are in the lowest parts of the flood plains of the streams of the region, they are naturally poorly drained and subject to annual overflow. Tile drainage is necessary before the lands can be utilized for anything but pasture.

2. EXPERIMENTAL TESTS

The pH values to be presented were obtained with a pH electrometer equipped with an inverted liquid junction especially adapted for making pH determinations of soils. A 1 to 1 soil-water ratio by volume was used for determining the pH of dried soils. Hereafter where reference is made to the pH of a dried soil, it will be understood that a 1 to 1 soil-water ratio was used in making the determination. During the measurements the calibration of the instrument was checked at frequent intervals against a standard buffer solution of known pH value.

A portion of the soil which had been obtained in the fresh, moist state and placed in air-tight containers was exposed to the atmosphere and allowed to dry. Measurements of the pH values made during the first two weeks showed no appreciable change. However, it is seen in table 1 that on exposure for 6 weeks, the samples became decidedly acid, with a change in pH value of 3.5 units in one sample, and 3.0 units in the other.

TABLE 1.—*Change in* pH *value on air-drying soil sample*

Duration of test	Sample 1	Sample 2
Days	pH	pH
0	7.2	7.2
27		6.2
38	3.7	
41		4.2

When the soil was dried, its color changed from black to grayish brown. A qualitative test of the fresh soil sample showed the presence of sulfides. A similar test on the aerated sample gave a negative test for sulfides. This showed that the sulfides present in the soil had been oxidized to sulfates on drying.

The changes in pH shown in table 1 are greater than any reported by previous investigators. However, the change from neutrality to high acidity on aerating soils is not entirely new, since such changes were detected as early as 1886 by Van Bemmelen [13], who showed that soils containing iron sulfide because of the reduction of sulfates by certain bacteria have an acid reaction on being aerated.

Van Bemmelen proved the presence in soils of pyrites and free sulfur formed by reduction of sulfates in the presence of ferric hydroxide. He states that P. J. Kerckhoff was the first to point out that these

acid soils contain ferrous sulfate, which was probably formed by the oxidation of iron sulfide. After further investigation, Van Bemmelen [13] ascribed the formation of acid in soil to the oxidation of iron sulfide in the form of pyrites. This oxidation results in the formation of ferric sulfate and sulfuric acid when air enters the soil. On hydrolysis, the ferric sulfate changes into yellow basic ferric sulfate and sulfuric acid. If acid soils become anaerobic again, the hydrogen-ion concentration would be expected to diminish gradually until a neutral reaction is attained because of resumption of the sulfate-reduction process.

In order to determine whether the pH value of the aerated sample could be made to return to the original value observed in the field, air-dried samples of the soil were ground and passed through a No. 20 mesh sieve. The soil was saturated with distilled water, which had been previously boiled to remove carbon dioxide, and placed in test tubes. After standing in boiling water for 15 minutes to force the entrapped air out of the saturated soil, the tubes were sealed. Determinations of pH were made on these stored samples over a period of several months. Table 2 shows the increases observed in the pH values on storing the samples. A second series in which the soil was treated with 3 ml of sodium lactate solution (containing 60 percent of sodium lactate) per 100 g of soil is represented by samples 6 and 7 in table 2. It was thought by supplying the sulfate-reducing bacteria with a suitable organic food, their activities might be increased. However, no change was detected by this procedure. Hence, it was assumed that enough organic food was present to favor the growth of the microorganisms.

TABLE 2.—*Increase in* pH *values of the air-dried samples upon saturation and exclusion of air*

Duration of test	Samples moistened with distilled water					Samples to which sodium lactate solution was added	
	1	2	3	4	5	6	7
Days	pH	pH	pH	pH	pH	pH	pH
0	3.9	4.0	4.0	4.0	3.8	4.0	4.0
15	4.9	-----	-----	-----	-----	-----	-----
25	-----	-----	-----	-----	-----	4.8	4.6
28	-----	5.1	5.1	-----	-----	-----	-----
29	5.1	-----	-----	-----	-----	-----	-----
38	-----	-----	-----	-----	6.3	-----	-----
39	-----	-----	-----	-----	-----	4.8	4.8
42	-----	6.0	-----	4.8	-----	-----	-----
49	6.2	-----	-----	-----	-----	-----	-----
54	-----	-----	-----	-----	-----	-----	4.8
57	-----	5.8	6.8	6.2	-----	-----	-----
68	-----	-----	-----	-----	-----	6.9	6.5
69	7.0	-----	-----	-----	-----	-----	-----
71	-----	6.4	7.1	6.2	-----	-----	-----
88	-----	-----	-----	-----	-----	7.2	7.0
91	-----	-----	-----	6.9	-----	-----	-----

It is seen in table 2 that the pH values of seven samples from the same soil ranged from 3.8 to 4.0 in the air-dried state. After saturation and exclusion of air over a maximum period of 3 months, the soils became approximately neutral. During the change in reaction

the color of the soil gradually changed from a grayish brown to a dark gray and finally to black.

Table 3 shows the effect of aeration on stored samples which had increased in pH value to near neutrality. On exposure to the atmosphere for 1 to 2 months, all the samples returned to the extremely acid condition, the pH values becoming approximately the same as those measured prior to treatment and sealing in the air-tight tubes.

TABLE 3.—*Effect of air-drying on the* pH *values of previously saturated samples*

Duration of test	Sample number						
	*1	2	3	4	5	6	7
Days	pH	pH	pH	pH	pH	pH	pH
0	7.0	6.4	7.1	6.9	6.3	7.2	7.0
3	-----	6.3	6.8	-----	-----	-----	-----
7	-----	-----	-----	6.5	-----	7.1	7.0
20	-----	4.4	4.8	6.0	-----	4.5	5.8
27	-----	4.1	3.9	-----	-----	-----	-----
30	-----	-----	-----	5.8	-----	4.2	3.9
39	4.4	-----	-----	-----	-----	-----	-----
49	-----	-----	-----	-----	3.4	-----	-----
59	-----	-----	-----	3.8	-----	-----	-----

* The sample number corresponds to the same sample reported in table 2. The pH values at 0 days in this table are the maximum values that the samples in table 2 reached.

The data in table 3 show that, on air-drying, reactions take place in the soil which result in a large increase in hydrogen-ion concentration. The data in table 2 indicate that with the exclusion of air from a saturated sample of the previously air-dried soil the reverse reaction takes place. Therefore, it is evident that with respect to pH, this particular soil can be passed through a cycle—from neutrality, as found in the natural field condition, to high acidity, which occurs in the air-dried state, and back to neutrality on resaturation and exclusion of air.

3. SIGNIFICANCE OF THE RESULTS WITH RESPECT TO CORROSION

The marked changes in acidity which have been described and the fact that sulfides were detected in the fresh, moist soil and not in the air-dried sample indicate a relation between the observed changes in pH values and the activity of sulfate-reducing anaerobic bacteria which are known to accelerate corrosion of metals buried in the soil. Under conditions favorable to their growth these bacteria possess the property of reducing sulfates present in the soil to sulfides. The importance of corrosion resulting from the activity of anaerobic bacteria was first reported by von Wolzogen Kühr [14, 15] in Holland. Subsequent investigations carried out by Bunker [16, 17] in England, and Hadley [18, 19, 20] in the United States are in agreement with the findings of von Wolzogen Kühr. Cultures of the bacteria have been prepared from products of corrosion on pipe lines and the bacteria have been studied under the microscope. These investigators have shown that, since the sulfate-reducing spirilla occur in practically every soil, the sulfate-reducing process is encountered throughout the world. The activity of the organisms is claimed to be one of the most

important causes of corrosion of iron and steel pipe in poorly drained anaerobic soils. Hadley [18] states that the importance of corrosion ascribed to sulfate-reducing bacteria is second only to that caused by stray-current electrolysis.

The conditions favorable to the growth of sulfate-reducing bacteria are (1) presence of moisture, (2) total absence of air (oxygen), (3) presence of assimilable organic compounds and necessary mineral substances (physiological elements), and (4) the presence of sulfate. Hadley [18] observed from investigations in swamps and lowlands that the pH of the soil water must be approximately 7.0 for the sulfate-reducing spirilla to be active. The limiting deviation noted from this value is ± 0.8 pH. Hence, other factors being favorable, measurement of pH is considered an important criterion in the identification of areas corrosive because of sulfate-reducing bacteria.

These bacteria, although becoming dormant in the presence of air, nevertheless require oxygen from some source for their physiological processes. Oxygen is available to the bacteria in the form of some oxygen-containing salt, the most common in soils occurring as sulfate.

In explaining the mechanism of the microbiological sulfate-reduction process with respect to corrosion, the general reaction whereby atomic hydrogen is removed from the cathodic areas may be expressed by the equation:

$$H_2SO_4 + 8H \longrightarrow H_2S + 4H_2O$$

By preventing polarization, this reaction permits corrosion to proceed uninterruptedly.

The sulfate-reducing bacteria can be expected to be active in poorly drained anaerobic soils where the soil shows a neutral reaction, if sufficient organic food and sulfates are present for the organisms to thrive on. These are generally soils of heavy texture (clay loams and clays) which would require artificial drainage if used for growing crops. The soils generally occupy flat areas and the water table is near or at the surface. The large changes in pH value between the fresh and air-dried soil samples that have been described occur under these same soil conditions.

IV. EFFECT OF SATURATION AND STORAGE WITH EXCLUSION OF AIR ON THE pH VALUES OF SOILS FROM CORROSION TEST SITES

The marked changes in pH shown by the Papakating soil raises the question whether similar changes might not be of more or less general occurrence in very poorly aerated soils. Since many soils show evidence of deficient aeration in the lower subsoil at the depths at which pipe lines are usually laid, some change in pH might be expected even in soils in which aeration is considerably better than is true of the Papakating soil. It is, of course, not to be expected that the relationship noted between changes in hydrogen-ion concentration and the oxidation and reduction of sulfur-containing salts would be observed generally, since many factors may produce changes in the pH values of soils over long periods of standing in contact with water with exclusion

of air. For example, increased concentration of ferrous ions resulting from the reducing process would be expected to increase the hydrogen-ion concentration because of hydrolysis of ferrous salts. With certain other classes of soils, namely those containing calcium carbonate or a high content of replaceable bases, production of hydrogen ions within the soil would not be expected to be reflected in appreciable change in hydrogen-ion concentration because of the large buffer action typical of such soils.

So far as the poorly drained soils are concerned, saturation of air-dried samples with consequent deoxidation would tend to restore the natural field condition of the soils. Hence, pH measurements made on soils which have stood in a saturated condition in the laboratory would be expected to represent more nearly the true pH value of the soils than measurements made directly on the dried samples. With well-aerated soils, on the other hand, saturation would undoubtedly exaggerate the changes in pH between the two states, and for this reason the method would not be so well adapted to this class of soils. However, in selecting soil samples for further study, it was considered worthwhile to include soils normally classified as well-aerated because of the corrosion which frequently occurs locally in such soils. Because of the wide range in properties shown by the soils in which the soil-corrosion test sites of the National Bureau of Standards are located [21, 22], samples of these soils are especially well adapted for the present study.

1. PROPERTIES OF SOILS

The properties of the soils shown in table 4 were taken from a previous publication [23].

TABLE 1.—*Properties of soils * in the National Bureau of Standards investigation*

TABLE 4.—*Properties of soils* [a] *in the National Bureau of Standards investigation*

[mg-eq = milligram equivalent]

A, Alkaline; G, good; F, fair; P, poor; VP, very poor.

Soil			Internal drainage of test site	Moisture equivalent	Resistivity at 60° F	Total acidity mg-eq per 100 g of soil	Composition of water extract, mg-eq per 100 g of soil						
No.	Type	Location					Na+K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
				%	*Ohm-cm*								
1	Allis silt loam	Cleveland, Ohio	*P*	28.6	1,215	11.4	0.72	0.25	0.43	0.00	0.09	0.09	0.83
2	Bell clay	Dallas, Tex	*P*	37.6	684	3.5	.28	1.09	.13	.00	1.18	.04	.18
3	Cecil clay loam	Atlanta, Ga	*G*	29.1	30,000	11.5							
4	Chester loam	Jenkintown, Pa	*G*	22.2	6,670	7.6							
5	Dublin clay adobe	Oakland, Calif	*P*	28.8	1,346	6.5	.93	0.48	.10	.00	0.69	.03	.25
6	Everett gravelly sandy loam	Seattle, Wash	*G*	12.2	45,100	12.8							
7	Maddox silt loam	Cincinnati, Ohio	*F*	34.3	2,120	29.8							
8	Fargo clay loam	Fargo, N. D	*P*	3.70	350	*A*	1.42	1.72	2.55	.00	.71	.01	4.43
9	Genesee silt loam	Sidney, Ohio	*P*	24.8	2,820	7.2							
10	Gloucester sandy loam	Middleboro, Mass	*F*	13.0	7,460	3.6							
11	Hagerstown loam	Baltimore, Md	*G*	32.0	11,000	10.8							
12	Hanford fine sandy loam	Los Angeles, Calif	*G*	12.4	3,190	2.5	0.39	0.50	0.16	.00	.40	.00	0.14
13	Hanford very fine sandy loam	Bakersfield, Calif	*F*	21.7	290	*A*	6.23	.09	.13	.00	1.12	1.64	3.76
14	Hempstead silt loam	St. Paul, Minn	*F*	17.2	3,520	5.6							
15	Houston black clay	San Antonio, Tex	*P*	51.4	489	5.0	2.18	.88	.20	.00	2.00	0.13	0.73
16	Kalmia fine sandy loam	Mobile, Ala	*F*	22.2	8,290	11.8							
17	Keyport loam	Alexandria, Va	*F*	30.8	5,980	19.1							
18	Knox silt loam	Omaha, Nebr	*G*	28.4	1,410	1.4	0.27	.63	.20	.00	0.94	.00	.25
19	Lindley silt loam	Des Moines, Iowa	*G*	28.4	1,970	10.9	.38	.32	.41	.00	.16	.03	.46
20	Mahoning silt loam	Cleveland, Ohio	*P*	22.4	2,870	1.5	.25	.48	.20	.00	.51	.00	.15
21	Marshall silt loam	Kansas City, Mo	*G*	31.2	2,370	9.5							
22	Memphis silt loam	Memphis, Tenn	*G*	28.4	5,150	9.7							
b23	Merced silt loam	Buttonwillow, Calif	*P*	24.7	278	*A*	8.38	.38	.22	.02	1.87	1.12	5.57
24	Merrimac gravelly sandy loam	Norwood, Mass	*G*	13.0	11,400	12.6							
25	Miami clay loam	Milwaukee, Wis	*F*	25.8	1,780	4.7	0.23	.70	.41	.00	1.01	0.03	0.10
26	Miami silt loam	Springfield, Ohio	*G*	16.4	2,980	2.6	.27	.50	.31	.00	0.70	.03	.12
28	Montezuma clay adobe	San Diego, Calif	*P*	24.6	408		1.50	0.6	.18	.00	.12	.99	.89
29	Muck	New Orleans, La	*VP*	34.5	1,270	28.1	2.15	1.92	1.55	.00	.00	1.69	2.30
30	Muscatine silt loam	Davenport, Iowa	*P*	29.4	1,300	2.6	0.32	0.65	0.40	.00	.71	0.09	0.24
31	Norfolk fine sand	Jacksonville, Fla	*G*	2.8	20,500	1.8							
32	Ontario loam	Rochester, N. Y	*G*	17.8	5,700	0.5	.23	.70	.12	.00	.73	.01	.42
33	Peat	Milwaukee, Wis	*VP*	72.8	800	36.0	1.52	7.30	4.06	.00		2.27	2.13
34	Penn silt loam	Norristown, Pa	*G*	23.4	4,900	7.0							
35	Ramona loam	Los Angeles, Calif	*F*	18.0	2,060	5.7	0.68	0.68	0.49	.00	1.10	0.06	0.35
36	Ruston sandy loam	Meridian, Miss	*G*	13.8	11,200	4.6							
37	St. John's fine sand	Jacksonville, Fla	*P*	7.0	11,200	15.3							
38	Sassafras gravelly sandy loam	Camden, N. J	*G*	3.0	38,600	1.7							
39	Sassafras silt loam	Wilmington, Del	*F*	24.2	7,440	6.6							
40	Sharkey clay	New Orleans, La	*P*	33.0	970	9.4	0.56	0.58	0.44	0.00	0.93	.07	0.28

TABLE 4.—*Properties of soils* [a] *in the National Bureau of Standards investigation*—Continued

[mg-eq=milligram equivalent]

A, Alkaline; G, good; F, fair; P, poor; VP, very poor.

Soil			Internal drainage of test site	Moisture equivalent	Resistivity at 60° F	Total acidity mg-eq per 100 g of soil	Composition of water extract, mg-eq per 100 g of soil						
No.	Type	Location					Na+K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
				%	*Ohm-cm*								
41	Summit silt loam	Kansas City, Mo	*F*	33.1	1,320	11.0	0.30	0.54	0.36	0.00	0.78	0.04	0.46
42	Susquehanna clay	Meridian, Miss	*P*	34.8	13,700	28.2							
43	Tidal marsh	Elizabeth, N. J	*VP*	55.4	60	36.8	45.10	5.17	9.45	.00	.00	43.30	37.00
44	Wabash silt loam	Omaha, Nebr	*G*	31.2	1,000	8.8	1.05	1.08	0.66	.00	1.97	0.82	0.41
45	Unidentified alkali soil	Casper, Wyo	*P*	14.8	263	*A*	8.15	3.70	.70	.00	0.24	.18	11.98
46	Unidentified sandy loam	Denver, Colo	*G*	7.6	1,500								
47	Unidentified silt loam	Salt Lake City, Utah	*P*	25.7	1,770	3.0	0.67	0.72	.39	.00	.88	.06	0.48
51	Acadia clay	Spindletop, Tex	*VP*	47.1	190	13.2	10.27	15.55	5.03	.00	.56	5.75	22.00
53	Cecil clay loam	Atlanta, Ga	*G*	33.7	17,794	9.6							
55	Hagerstown loam	Baltimore, Md	*G*	32.0	5,213	10.9							
56	Lake Charles clay	El Vista, Texas	*P*	28.7	406	4.5	3.12	0.69	0.47	.00	.80	1.59	3.04
58	Muck	New Orleans, La	*VP*	57.8	712	79.3	2.03	2.23	1.29	.00	.00	0.47	2.54
59	Carlisle muck	Kalamazoo, Mich	*P*	43.6	1,659	33.3	1.03	3.08	2.70	.00	.00	3.47	1.04
60	Rifle peat	Plymouth, Ohio	*VP*	43.4	218	297.4	2.91	10.95	2.86	.00	.00	.00	56.70
61	Sharkey clay	New Orleans, La	*P*	30.8	943	8.6	0.73	0.68	0.33	.00	.71	.10	0.91
62	Susquehanna clay	Meridian, Miss	*P*	34.6	6,922	24.2							
63	Tidal marsh	Charleston, S. C	*VP*	46.7	84	100.2	33.60	6.85	4.00	.00	.00	12.70	36.60
64	Docas clay	Cholame, Calif	*VP*	41.1	62	*A*	28.10	2.29	0.76	.00	.89	28.80	0.26
65	Chino silt loam	Wilmington, Calif	*F*	26.4	148	*A*	7.65	12.40	2.20	.00	1.30	6.05	16.90
66	Mohave fine gravelly loam	Phoenix, Ariz	*G*	16.5	232	*A*	6.55	0.51	0.18	.00	0.73	2.77	2.97
67	Cinders	Milwaukee, Wis	*VP*	11.1	455	*A*	0.77	3.03	.53	.00	.55	0.08	2.89
[b] 70	Merced silt loam	Buttonwillow, Calif	*P*	24.7	278	*A*	8.38	0.38	.22	.02	1.87	1.12	5.57
72	Papakating silty clay loam	Yale, Ohio	*VP*		762								

[a] Measurements and determinations by I. A. Denison and R. B. Hobbs.
[b] The soils are from the same test site.

2. EXPERIMENTAL TESTS

Two samples of each of 62 air-dried soils were saturated with previously boiled distilled water and placed in test tubes or small bottles. After allowing the tubes to stand in boiling water for 15 minutes to force the entrapped air out of the saturated soil, 10 to 15 ml of distilled water was added and the tubes sealed and stored. Measurements of pH and a qualitative test for the presence of sulfides were made on the air-dried samples before the treatment was applied. No sulfides were found in any of the air dried samples. Measurements of pH were made on the stored samples after approximately 120 and 350 days. At the end of the 350-day period the samples were also tested for the presence of sulfides.

3. COMPARISON OF pH VALUES OF AIR-DRIED AND DEAERATED SAMPLES

(a) VERY POORLY AND POORLY DRAINED SOILS

The effect of deaeration on the pH values of the very poorly and poorly drained soils is shown in tables 5 and 6. The muck soils (29 and 58), the peat (33), and the very heavy Acadia clay (51) show the trend noted in the case of the Papakating soil with respect both to marked increase in hydrogen-ion concentration and reduction of sulfates to sulfides. Since these soils contain an abundance of organic matter and sulfates and have pH values close to neutrality, the environmental conditions are well adapted for supporting the activity of anaerobic bacteria. The tidal marsh soils (43, 63A, and 63B) and the peat soils (60A and 60B) contain in abundance the essential elements required for sulfate-reduction, namely organic matter and sulfates, but their pH values ranging from 2.87 to 3.45 are too low to permit bacterial activity. This is indicated by the lack of change in pH.

TABLE 5.—*Change in* pH *values of air-dried samples upon saturation and exclusion of air*

[Drainage of soils, very poor]

Soil [a] number	pH of air-dried sample	pH after saturation and exclusion of air		Change in pH after 350 days
		120 days	350 days	
29	3.75	----	[b] 5.98	+2.23
33	6.40	7.28	[b] 7.36	+0.96
43	3.45	3.40	3.42	− .03
51	5.10	5.99	[b] 6.05	+ .95
58A	4.53	5.87	6.18	+1.65
58B	4.35	5.20	6.25	+1.90
60A	2.21	----	2.54	+0.33
60B	2.25	2.20	2.81	+ .56
63A	3.05	3.10	3.00	− .05
63B	2.87	2.86	3.04	+ .17
64	7.75	7.46	6.99	− .76
76	8.60	8.50	7.50	−1.10
72	3.78	6.34	[b] 6.98	+3.20

[a] See table 4 for soil type, locations, and properties of the soils.
[b] These samples gave a positive test for sulfides.

TABLE 6.—*Change in* pH *values of air-dried samples upon saturation and exclusion of air*

[Drainage of soils, poor]

Soil number	pH of air-dried sample	pH after saturation and exclusion of air		Change in pH after 350 days
		120 days	350 days	
1	4.56	4.58	4.55	−0.01
2	6.70	7.14	*7.10	+.40
5	5.75	7.14	*7.02	+1.27
8	7.81	7.29	*6.98	−0.83
9	6.90	6.96	*7.35	+.45
15	7.30	7.19	*7.35	+.05
20	5.75	5.98	5.94	+.19
23	8.88	7.65	6.90	−1.98
28	3.99	4.31	4.90	+0.91
30	6.62	6.62	6.58	−.04
37	3.72	4.22	4.19	+.47
40	6.27	7.35	7.31	+1.04
42	4.36	4.82	4.35	−0.01
45	8.22	7.47	*6.80	−1.42
47	7.92	7.58	*7.05	−0.87
56	7.22	7.23	*7.24	+.02
59	5.66	6.30	6.45	+.79
61	6.22	7.03	7.03	+.81
62	4.07	4.12	4.10	+.03
70	8.71	7.58	6.72	−1.99

* These samples gave a positive test for sulfides.

The Houston black clay (15) and Lake Charles clay (56) have undergone sulfate-reduction without any appreciable change in hydrogen-ion concentration. These soils contain either calcareous material or very high contents of absorbed bases and no change in pH from reduction of sulfates would be anticipated. In order for an increase in hydrogen-ion concentration to take place on air-drying, there must be a low buffer capacity in the soil. Hissink [24] states that the formation of acid due to the oxidation of accumulated sulfides can produce higher degrees of acidity only if there are no basic elements present in the soil. Hence, if a soil is plentifully supplied with bases, e. g., soils of high lime content, the oxidation of the sulfides to sulfates may cause no significant change in reaction.

The behavior of the poorly drained soils from sites 2, 5, and 9 (table 6) is in general agreement with the trend that has been noted. In some samples, such as soils 8, 45, and 47, which were alkaline in the air-dried state, sulfate-reduction has occurred accompanied by an increase in hydrogen-ion concentration. The highly alkaline Merced silt loam samples, soils 23 and 70, showed a decrease in pH value by almost 2.0 units. This is probably due to the removal of sodium carbonate by reaction with calcium or magnesium ions brought into solution over long periods of standing.

In the case of the acid soils 1, 30, and the two Susquehanna samples (42 and 62), deoxidation has resulted with no significant change in hydrogen-ion concentration.

(b) WELL-DRAINED SOILS

The changes in pH values undergone by the generally well-drained soils are shown in tables 7 and 8. As has been stated, the purpose of the treatment to which the air-dried samples were subjected, namely, saturation and storage with exclusion of air, was to restore the natural

condition of the soil. Obviously this condition has not been realized for the class of well-aerated soils under consideration, because a deoxidized condition has been substituted for the normal oxidized state. For this reason, for the soils listed in tables 7 and 8 the method is too drastic. However, it has been observed [25] that severe corrosion often occurs locally in soils of normally good drainage where corrosion ordinarily would not be predicted. Corrosion in such soils does not occur generally throughout the soil type, but is confined to restricted areas of deficient aeration that are too small in their extents to be properly classified. Mottling close to the surface may usually be found in such areas. These local areas in which reduction by bacterial processes would be expected to occur might be entirely overlooked if pH measurements were confined to air-dried samples.

TABLE 7.—*Change in* pH *values of air-dried samples upon saturation and exclusion of air*

[Drainage of soils, fair]

Soil number	pH of air-dried sample	pH after saturation and exclusion of air		Change in pH after 350 days
		120 days	350 days	
7	4.55	4.30	.....	.....
10	4.63	5.25	5.35	+0.72
13	10.56	9.25	*7.90	−2.66
14	7.31	6.93	5.95	−1.36
16	4.75	6.39	6.92	+2.17
17	4.20	5.30	5.45	+1.25
25	7.73	7.33	*7.23	−0.50
35	7.53	7.70	7.20	−.33
39	4.94	5.50	5.45	+.56
41	7.24	7.45	*7.20	−.04
65	8.06	7.28	*7.19	−.87

* These samples gave a positive test for sulfides.

TABLE 8.—*Change in* pH *values of air-dried samples upon saturation and exclusion of air*

[Drainage of soils, good]

Soil number	pH of air-dried sample	pH after saturation and exclusion of air		Change in pH after 350 days
		120 days	350 days	
3	4.82	5.76	5.94	+1.12
4	4.60	5.54	5.57	+0.97
6	4.85	5.86	6.42	+1.57
11A	5.71	.....	5.80	+0.09
11B	6.22	6.75	7.15	+.93
12	6.73	7.52	7.70	+.97
18	7.03	7.60	7.70	+.67
19	4.91	5.89	5.76	+.85
21	5.95	6.56	*6.65	+.70
22	4.88	5.06	5.30	+.42
24	5.18	5.88	5.50	+.32
26	7.60	7.51	6.55	−1.05
31	5.60	6.12	6.15	+0.55
32	7.62	7.40	7.45	−.17
34	5.86	6.50	5.91	+.05
36	5.20	6.52	*6.49	+1.29
38	4.59	4.82	6.10	+1.60
44	6.13	6.91	6.35	+0.22
46	7.00	6.94	6.93	−.07
53	4.80	5.39	5.13	+.33
55	5.94	6.18	6.53	+.59
66	8.84	8.05	8.20	−.64

* These samples gave a positive test for sulfides.

V. DISCUSSION

The pH values measured after storage in the saturated condition represent extreme values which might be expected in nature if the soils should become completely deaerated over a long period. Since few of the soils at the corrosion test sites are known to be in this condition except temporarily, the values presented for the saturated soils cannot be considered as replacing values of pH previously reported, although there is no doubt that the values in the moist condition represent more nearly the pH of at least the very poorly aerated soils in their field condition. However, the data clearly indicate that the true pH of many of the soils can be measured accurately only with the soil in the field condition. If the measurements are to be made in the laboratory, the samples must obviously be preserved in the natural field condition. It is planned at a convenient time to measure the pH values of soils at the corrosion test sites according to the revised procedure.

As it has been shown that the pH of soils is subject to variation depending on variations in climate and other factors [7, 11, 12], the recommended procedure of measuring the pH of soils under field conditions raises the question of reproducibility. Some degree of reproducibility will almost certainly be sacrificed, but this loss will be more than offset by the gain in accuracy obtained at least in the case of the poorly drained soils.

In view of the data presented, it can be concluded that for the identification of areas corrosive to iron and steel it is preferable to measure the pH of soils in their natural condition or on samples maintained in the field condition. Unless the pH of soils is properly measured, the conclusion is likely to be drawn that corrosion resulting from bacterial activity in some soils is unimportant, whereas, it may, in fact, be particularly severe.

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RESEARCH PAPER RP1640

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SPECIFIC HEATS OF GASEOUS 1,3-BUTADIENE, ISOBUTENE, STYRENE, AND ETHYLBENZENE

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ABSTRACT

This paper describes a flow calorimeter and measurements of the specific heats of four hydrocarbons that are of interest in connection with synthetic rubber. The measurements on gaseous 1,3-butadiene and isobutene cover the range −35° to +80° C. The specific heats of styrene vapor and ethylbenzene vapor were determined at 100° C. The calorimeter was tested by measuring the specific heat of normal hydrogen. The results on the hydrocarbons are believed to be correct to ±0.5 percent.

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I. INTRODUCTION

The measurements described in this paper were undertaken at the Bureau as part of a program of obtaining thermal data on the properties of materials of interest in connection with synthetic rubber. The compounds studied in the present investigation are among the most important of the materials used in the synthetic-rubber industry. Butadiene and styrene are the principal ingredients of GR–S (Government rubber-styrene type). Isobutene is copolymerized with isoprene in the manufacture of butyl rubber. Ethylbenzene is converted into styrene by dehydrogenation, this process supplying most of the styrene used.

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The calorimeter used was of the adiabatic constant-flow type designed to have a small resistance to flow so that measurements could be made on vapors of low saturation pressure. The specific heats of gaseous butadiene and isobutene were measured at four temperatures between −35° and 80° C. Because of the low vapor pressures of styrene and ethylbenzene, the specific heats of their vapors were measured at only one temperature, 100° C. The apparatus was tested by measuring the specific heat of normal hydrogen.

The specific-heat data obtained are useful for comparison with calculations of thermodynamic properties based on spectroscopic data, calculations which were made to extend to higher temperature tables of calorimetric properties determined at low temperatures.

II. MATERIALS

The samples of hydrocarbons used in this investigation were obtained from several different sources. The impurities in the various samples are believed to be so small as to have a negligible effect on the specific heat results. The sources and estimated purities of the samples are given below.

1. BUTADIENE

The 1,3-butadiene was furnished by the Dow Chemical Co. It was stated to contain about 0.2 mole percent of impurity. A small amount of polymer in the liquid would not affect the results because the vapor was supplied to the calorimeter from a boiler, and the polymer of low vapor pressure would remain in the boiler. This applies also to isobutene and styrene.

2. ISOBUTENE

The isobutene was furnished by the Standard Oil Development Co. The purity of the sample used was not directly determined, but measurements on other samples from the same cylinder indicated that its purity was higher than 99 mole percent.

3. STYRENE

The styrene was supplied by the Dow Chemical Co. The liquid soluble, solid insoluble, impurity calculated from the freezing point was 0.75 mole percent. Tertiary-butyl-catechol (0.005 percent by weight) was added to the liquid to reduce the rate of polymerization.

4. ETHYLBENZENE

The ethylbenzene was part of a sample distilled by M. R. Fenske of the Petroleum Refining Laboratory of The Pennsylvania State College. The physical constants reported by The Pennsylvania State College were: 50 percent, Cottrell boiling point 136.25° C; index of refraction $n_D^{20}=1.4958$. The freezing point, measured by Alfred Matuszak at American Petroleum Institute Laboratories of Ohio State University was −95.02° C. The amount of impurity in this sample appears to be of the order of 0.2 mole percent.

III. APPARATUS

The calorimeter used for this investigation was of the constant flow, adiabatic type. Some important features of design were adapted from the flow calorimeter of Osborne, Stimson, and Sligh [1].[1] Simplifications were introduced to make the construction less difficult. The resistance to flow was reduced so that gases of low saturation pressure could be passed through the calorimeter at satisfactory rates. The maximum pressure drop through the calorimeter during the present experiments was 46 millimeters of mercury, observed when passing butadiene through the calorimeter at a mean pressure of 90 millimeters of mercury, at a rate of 1 gram per minute. The heat capacity of the internal part of the calorimeter was kept small to facilitate the establishment of thermal equilibrium with a small flow of gas. As it was desired also to measure the specific heat of vapors (other than hydrocarbons) that corrode copper and silver, the use of these metals was avoided in the construction of certain parts of the calorimeter. This was a disadvantage, since the high thermal conductivity of copper or silver is desirable where isothermal surfaces are wanted. All parts of the apparatus traversed by the gas are made of monel tubing of 0.010-inch wall thickness.

Figure 1 is a scale diagram of the principal parts of the apparatus. The calorimeter is immersed in the bath, B, the temperature of which is controlled by supplying electric power to the heater, H_b. The propeller, P, forces the liquid down through the tube, T_1. On the outside of this tube near the bottom is the resistor, R, consisting of about 140 ohms of No. 37 AWG copper wire, which forms one arm of a Wheatstone bridge circuit. The galvanometer in this circuit will respond to a change in temperature of the bath of less than 0.001° C, and it is not difficult, by manual control, to keep the bath temperature constant to 0.002 or 0.003 degree centigrade. The arrangement shown at the left side of the diagram is used to cool the bath when operating below room temperature. It consists of a copper rod, CR, which conducts heat from the bath into the liquid air, A. Vanes of sheet copper are soldered to each end of the rod to improve thermal contact with the liquids. The brass tube, C, closed at the bottom prevents the liquid air from coming into contact with the copper rod, except at the lower end. This makes the rate of heat transfer almost independent of the depth of the liquid air.

The gas being investigated enters at I and passes through the helical tube, T_2, where it is brought to the temperature of the bath. The tube, T_2, enters the evacuated chamber at the bottom. The gas passes through a system of baffles in the tube and then is heated by the calorimeter heater, H_c, which consists of about 14 ohms of No. 34 AWG constantan wire with fiber-glass insulation. At this point the direction of flow of the gas is reversed so that it passes down through the annular space surrounding the heater. The heater is not in the gas stream but lies between the two inner coaxial tubes. The gas then enters the outside annular space and flows upward again and enters the small part of the tube where it passes through another system of baffles. By the time the gas reaches this region any nonuniformity in temperature, which may have existed near the heater,

[1] Figures in brackets indicate the literature reference at the end of this paper.

should have disappeared. The baffles in the tube are intended to obstruct radiation along the tube and to promote thermal equilibrium between the gas stream and the wall of the tube. The gas leaves the calorimeter through the throttle valve, *V*.

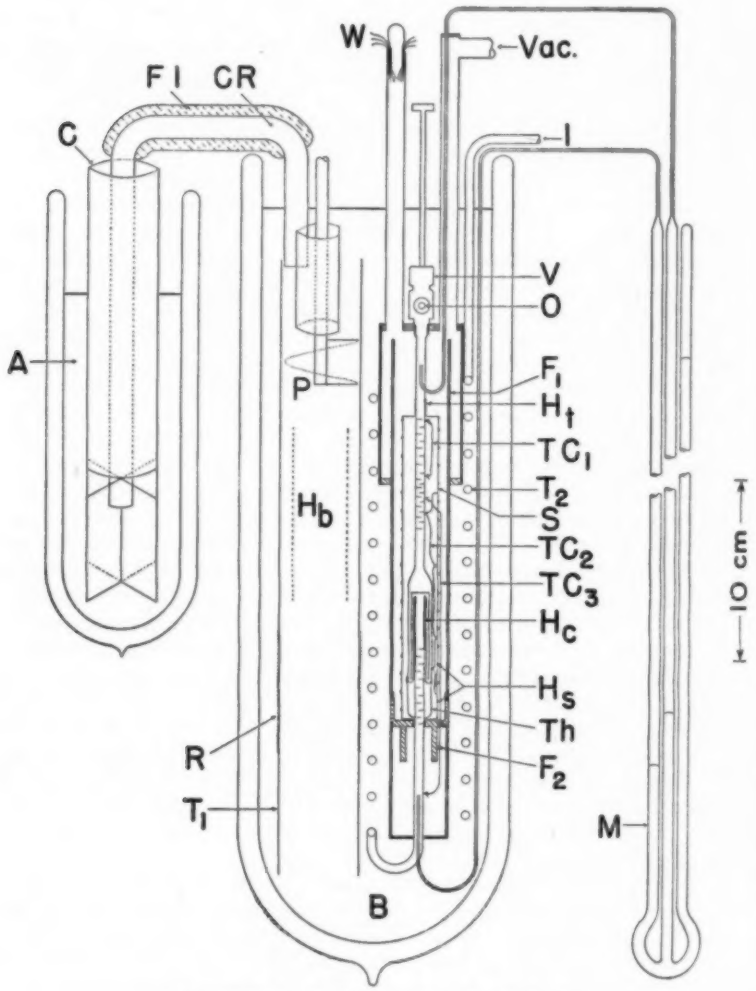

FIGURE 1.—*Scale diagram of calorimeter.*

A, Liquid air; *C*, protecting cylinder; *FI*, felt insulation; *CR*, copper rod; *P*, propeller; H_b, H_t, H_c, and H_s, electric heaters; *R*, copper resistor; T_1, stirrer tube; *W*, wax seal; *Vac*, vacuum line; *I*, inlet; *V*, throttle valve; *O*, outlet; F_1, flange; TC_1, TC_2, and TC_3, thermocouples; T_2, helical tube; *S*, radiation shield; Th, metal thimble; F_2, flange; *B*, constant temperature bath; *M*, manometer.

The labyrinth which the gas traverses after passing the heater is for the purpose of obtaining an isothermal exterior surface on this part of the calorimeter. The metal thimble, T_h, extends this isothermal surface to a point very close to where the tube enters the

copper radiation shield, S. This shield is heated to the temperature of the inner adjacent wall of the calorimeter by means of the electric heater, H_s, the necessary adjustments being indicated by the three-junction chromel-constantan thermocouple, TC_2. Where the ends of the radiation shield approach to within about one-half millimeter of the tube conducting the gas, metallic contact with the tube is avoided and the shield is supported by a lacing of cotton cord passing through four small holes in each end and around the edges of the center hole.

The rise in temperature of the gas is measured by the five-junction copper-constantan thermocouple TC_3. The wires of this couple make three turns around both the radiation shield and flange F_2 and are cemented with Glyptal lacquer so that they are brought nearly to the correct temperatures before the junctions make thermal contact with the calorimeter tube. The tube heater, H_t, is for the purpose of establishing a zero temperature gradient in the upper part of the tube, the gradient being indicated by the thermocouple, TC_1. All the electrical leads to the heaters and thermocouples enter the vacuum chamber through the wax seal, W, and are brought close to the temperature of the bath by being wound around the flange, F_1.

The pressure of the gas, before and after heating, is measured by means of the manometer, M. The manometer could not be used for the measurements on styrene and ethylbenzene because these materials would have condensed on the surfaces that were at room temperature. During the experiments on these substances the manometer was removed, and the metal connecting tubes were closed by soldering in wires that fit the tubes closely, so that there was very little unoccupied volume in the parts of the tubes, which were at room temperature.

IV. METHOD

The measurements consisted of determinations of the rate of flow, r, of the gas through the calorimeter, the electric power, W, to the calorimeter heater, and the rise in temperature of the gas, Δt. Because of the pressure drop through the calorimeter and the resultant Joule-Thomson cooling, it was necessary to make auxiliary measurements of the decrease in temperature, δt, of gas flowing through the calorimeter, when no power was supplied to the calorimeter heater, H_c. The specific heat of the gas, C_p, at the mean pressure and temperature of the experiment was computed by the relation

$$C_p = \frac{W}{r(\Delta t + \delta t)}.$$

A constant rate of flow of gas was attained by maintaining a constant pressure on the inlet side of the calorimeter and a constant pressure difference between the inlet and outlet. At the start of a measurement the desired rate of flow was obtained by adjusting the throttle valve, V. In the experiments with hydrogen the outlet pressure was atmospheric and the inlet pressure was kept at the desired value above atmospheric by supplying hydrogen from a cylinder through a reducing valve and allowing some of the hydrogen to escape, before entering the calorimeter, by bubbling through a depth of water. In the experiments with the hydrocarbons the inlet pressure was kept constant by controlling the electric power supplied to an external boiler, which

supplied vapor to the inlet of the calorimeter. The outlet pressure was kept very low by condensing the compound in a cold reservoir.

The rate of flow of hydrogen was measured by means of a laboratory wet test gas meter, which could be read to 0.001 cubic foot. This meter was calibrated by the Weights and Measures Division of this Bureau. The hydrogen, before entering the calorimeter, was dried by passing through a cotton filled U-tube cooled with liquid air. After leaving the calorimeter and before entering the gas meter, the hydrogen bubbled through water. This improved the approach to saturation [2] and reduced the amount of water carried out of the meter by the gas. The rates of flow of the hydrocarbons were determined by weighing the amounts collected in the condensing reservoir during measured intervals of time.

The power input to the calorimeter was determined by measuring the current flowing through the heater and the potential drop across the heater. A Wenner potentiometer, together with a volt box and a standard resistor were used for these measurements. The electromotive force of the thermocouple, TC_3, which is used to determine the temperature rise Δt and the Joule-Thomson, δt, was also measured with the Wenner potentiometer. This thermocouple was calibrated, before assembling the calorimeter, by comparison with a standard platinum resistance thermometer.

During the measurements on hydrogen, butadiene, and isobutene, the pressure of the gas, before and after heating, was measured with the manometer, M, (fig. 1). Since the manometer could not be used for measurements on styrene and ethylbenzene it was necessary to calculate the pressures. The ingoing pressure was assumed to be the vapor pressure corresponding to the temperature of the boiler (90° C). The pressure drop in the calorimeter was calculated by means of the relation

$$\Delta p = k\rho V^2,$$

where Δp is the pressure drop, k is a constant, ρ is the density of the gas, and V is the volume rate of flow of gas through the calorimeter. This relation is approximately correct for turbulent flow. The constant, k, was evaluated from measurements on air.

The time required to establish steady conditions, after adjusting the rate of flow and the power input, varied from 20 to 40 minutes, depending upon the rate of flow. After steady conditions were established, measurements of power, temperature rise, and rate of flow were made for periods of from 10 to 30 minutes.

V. TEST OF THE CALORIMETER WITH HYDROGEN

Auxiliary measurements of the specific heat of normal hydrogen were carried out in order to obtain additional information about the accuracy of measurements obtained with this calorimeter. Hydrogen was chosen for this purpose because values of specific heat calculated from spectroscopic data are believed to be trustworthy and there was available an ample supply of material of adequate purity.

Hydrogen was generated electrolytically and stored in a high-pressure cylinder. Earlier analyses of the dried hydrogen prepared in the same way showed an impurity of less than 0.02 mole percent. The

hydrogen was passed through the calorimeter at a pressure slightly above atmospheric. The rates of flow range from 2 to 9 moles per hour for the various measurements. The power input to the calorimeter was usually adjusted to produce a temperature rise of about 10 degrees centigrade although in one case the rise was only 6 degrees. No Joule-Thomson heating was detectable for the rates of flow used in these experiments.

The mean temperatures of the four series of measurements were −29°, 42°, 80°, and 100° C. Upon comparing the observed values with those calculated from spectroscopic data, it appeared that most of the meaured values were a little low and that the discrepancy was greater for small rates of flow. In order to correlate the data for different rates of flow, the differences (in percent) between the observed and spectroscopic values were plotted as ordinates with values of $\Delta t/W$ as abscissas, where Δt is the temperature rise of the gas as it flows through the calorimeter, and W is the power input causing the temperature rise. If the heat lost or gained, because of failure to establish strictly adiabatic conditions, is assumed to be proportional to Δt, $\Delta t/W$ will be proportional to the fractional error in specific heat caused by the loss or gain of heat. For a given gas, if t and Δt are kept constant, $\Delta t/W$ is inversely proportional to the rate of flow. The use of the quantity $\Delta t/W$, rather than the reciprocal of the rate of flow, permits the correlation of data on different materials and with different values of Δt.

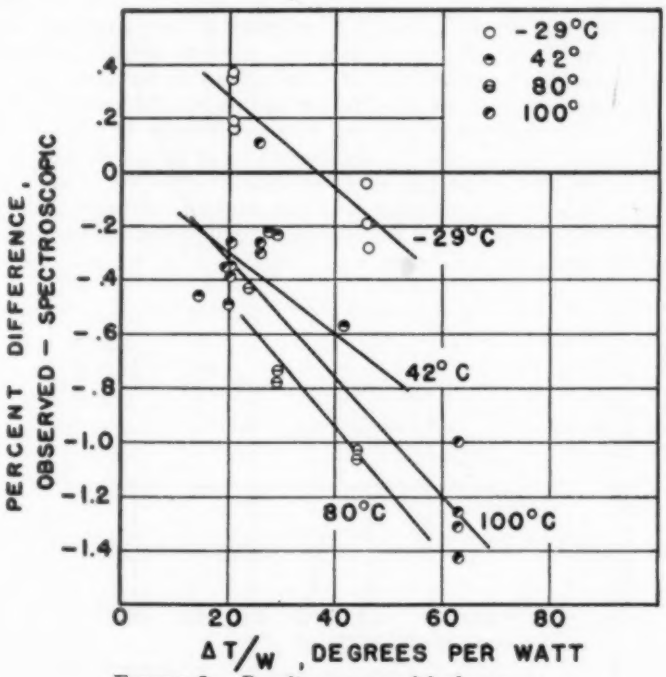

FIGURE 2.—*Results on normal hydrogen.*

Differences, in percent, between observed values of specific heat and those calculated from spectroscopic data, plotted as functions of $\Delta t/W$, the ratio of temperature rise to power input.

Figure 2 shows the correlation for the data on hydrogen. The spectroscopic values of specific heat used are given in table 1. A calculation showed that the difference between the specific heat of hydrogen at 1 atmosphere and in the ideal gas state amounted to only 1 part in 6,000 and hence could be neglected.

TABLE 1.—*Specific heat of normal hydrogen calculated from spectroscopic data*[a]

t	C°_p
° C	*cal mole⁻¹ deg⁻¹*
−29	6.750
+42	6.917
+80	6.955
+100	6.966

[a] Interpolated from an unpublished table prepared by H. W. Woolley and F. G. Brickwedde.

Although there is a considerable amount of scattering of the individual observations shown in figure 2, it is evident that there is a systematic deviation which depends upon the temperature and upon the value of $\Delta t/W$. Because of the apparent regularity of the deviation, it appeared possible to use the results on hydrogen to apply corrections to the values of specific heat obtained for other gases, although the original purpose of the measurements on hydrogen was to test the accuracy of measurements obtained with this calorimeter. To achieve this result the following correlation was made. The straight line isotherms were drawn in figure 2 to represent the error as a function of $\Delta t/W$ at the different temperatures. Except for the −29 degree isotherm, these lines appear to be directed so as to pass close to the origin. It was hoped that all the isotherms would pass through the origin, since the value zero for $\Delta t/W$ corresponds to infinite rate of flow, and under this condition accidental heat losses should be negligible. It is possible that the measurements at −29° C were subject to an effect which did not appear at the higher temperatures. However, there does not seem to be any justifiable method of making the −29 degree isotherm conform, so it was decided to use the data as

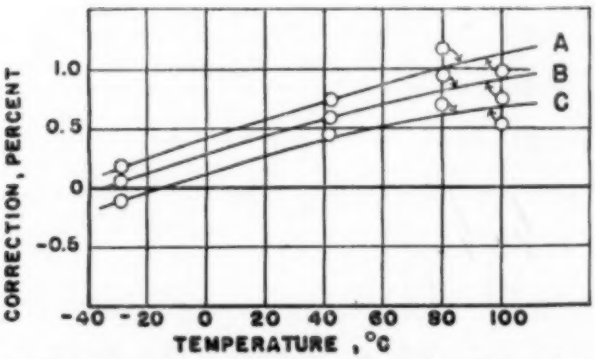

FIGURE 3.—*Correction chart showing percentage to be added to observed values of specific heat*

A, $\Delta t/W$=50 deg per watt; *B*, $\Delta t/W$=40 deg per watt; *C*, $\Delta t/W$=30 deg per watt.

they stand. Values of the ordinate (fig. 2) were read off at each temperature for values of $\Delta t/W$ of 30, 40, and 50 degrees per watt. The negatives of these values were plotted as functions of temperature in figure 3, the resulting graph being used for the correction of observations on the other compounds.

VI. RESULTS

Table 2 gives the magnitudes of the quantities observed during the measurements of the specific heats of the hydrocarbons. Also shown are magnitudes of $C_p - C_p^\circ$, the difference between the specific heat of the gas at the observed pressure and the specific heat in the ideal state. Values of $C_p - C_p^\circ$ were calculated by means of the relation

$$C_p - C_p^\circ = \frac{81 R_p T_c^3}{32 p_c T^3},$$

in which R is the gas constant, p is the pressure, T is the observed temperature, and T_c and p_c are the critical temperature and pressure, respectively. This relation is derivable from the Berthelot equation of state and the exact thermodynamic relation

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p.$$

T and T_c are in degrees Kelvin, equal to t° C plus 273.16. The values used for p_c and T_c are given in table 3.

TABLE 2.—*Magnitudes of quantities involved in the determinations of the specific heats of 1,3-butadiene, isobutene, styrene, and ethylbenzene*

Material	Temperature	Number of observed points	Rate of flow		Temperature rise, Δt		Joule-Thomson effect		Pressure	$C_p - C_p^\circ$
			Minimum	Maximum	Minimum	Maximum	Minimum	Maximum		
	°C		g sec⁻¹	g sec⁻¹	°C	°C	% of Δt	% of Δt	mm Hg	% of C_p
1,3-Butadiene	−35.0	4	0.0085	0.016	9.9	11.6	0.6	2.4	90	0.5
	0.0	5	.013	.024	9.6	9.8	.4	1.3	280	.9
	40.0	5	.015	.021	9.3	9.6	.4	0.8	290	.6
	80.0	4	.008	.021	8.9	9.1	.2	.8	280	.4
Isobutene	−34.0	5	.011	.015	8.4	9.4	1.1	2.1	90	.4
	−1.0	2	.016	.016	8.3	8.3	0.2	0.2	295	.9
	39.0	6	.007	.018	8.7	9.4	.2	.4	290	.5
	80.0	4	.009	.018	7.9	8.1	.1	.6	295	.3
Styrene	100.0	7	.010	.016	10.3	12.3	.6	1.5	125	.3
Ethylbenzene	100.0	7	.008	.020	8.8	10.6	.2	1.5	175	.4

TABLE 3.—*Values of the critical constants used in calculating the values of* $C_p - C_p^\circ$

Material	p_c	T_c	Reference
	atm	°K	
1,3-Butadiene	42.87	426	Meyers, Scott, Brickwedde, and Rands [3].
Isobutene	39.48	417.9	Beattie, Ingersoll, and Stockmayer [4].
Styrene	36.3	639	Calculated [5].
Ethylbenzene	36.9	619.5	Altschul [6].

Table 4 gives the results of the specific heat measurements on the hydrocarbons. The values given in column 4 are the weighted means of the experimental values, greater weight being given to measurements made with high rates of flow. A correlation similar to that used for the hydrogen data was not satisfactory. In most cases the observed values failed to show a definite trend or dependence on the value of $\Delta t/W$. It seems likely that the trend was masked by the scattering of the individual observations, and that much more data would be required to show a trend in every series of measurements.

Column 5 of table 4 gives the average of the absolute magnitudes of the deviations of the experimental values from the mean value given in column 4. In view of the results on hydrogen it is believed that the values given in column 4 are likely to be low, and that they would be improved by applying the corrections indicated by the hydrogen data. The corrections given in column 7 were obtained from figure 3. The last column shows the corrected values of C_p°, the specific heat in the ideal gas state.

TABLE 4.—*Specific heats in the ideal gas state.*

[Summary of results, including corrections resulting from the test of the calorimeter with hydrogen. 1 calorie = 4.1833 international joules.]

Material	Temperature	Number of observations	$C_p - C_p^\circ$	C_p° weighted mean	ΔC_p° average deviation from weighted mean	$\Delta t/W$	Correction	C_p° corrected
	°C		cal mole^{-1} deg^{-1}	cal mole^{-1} deg^{-1}	cal mole^{-1} deg^{-1}	deg watt^{-1}	%	cal mole^{-1} deg^{-1}
Butadiene	−35.0	4	0.08	15.72	0.04	50	0.13	15.74
	0.0	5	.16	17.64	.04	30	.12	17.66
	40.0	5	.11	19.95	.03	30	.41	20.03
	80.0	4	.08	22.11	.03	30	.62	22.25
Isobutene	−34.0	5	.08	18.10	.08	50	.14	18.12
	−1.0	2	.18	19.76	.01	40	.27	19.81
	39.0	6	.12	21.78	.03	40	.58	21.91
	80.0	4	.08	23.76	.03	40	.84	23.96
Styrene	100.0	7	.11	35.83	.07	40	.92	36.16
Ethylbenzene	100.0	6	.16	37.71	.07	40	.92	38.06

VII. ESTIMATE OF ACCURACY

The only reliable evidence concerning the accuracy of the results is contained in the measurements of the specific heat of hydrogen. If the individual observations on hydrogen had been simply averaged at each temperature, the greatest difference between the observed mean values and the spectroscopic values would have been 0.8 percent. Although the values obtained for the hydrocarbons were corrected by making use of the data on hydrogen, it is too optimistic to assume that the systematic error was entirely eliminated, since it has not been proved that the error is independent of the nature of the gas being investigated. However, it is reasonable to expect that making the corrections resulted in some improvement. Therefore, it is the authors' opinion that errors in the corrected values given in table 4 are probably less than 0.5 percent.

VIII. COMPARISON WITH WORK OF OTHER OBSERVERS

While this paper was being prepared for publication two articles appeared that reported measurements of the specific heat of butadiene vapor. In the first of these papers, by Aston, Moessen, Hardy, and Szasz [7], the specific heats were computed from measurements of the velocity of ultrasound. The second paper, by Templeton, Davies, and Felsing [8], reported calorimetric measurements. Figure 4 shows the data of the different observers. A line was drawn through the data

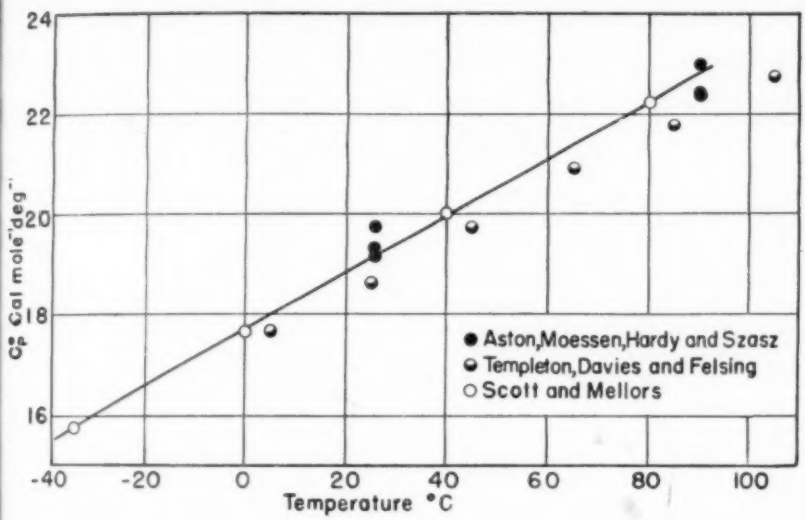

FIGURE 4.—*Specific heat of 1,3-butadiene vapor.*

Comparison of values obtained by different observers. The solid circles showing the data of Aston, Moessen, Hardy, and Szasz do not represent three separate determinations at each temperature, but result from three different methods of computing specific heats from a single series of experimental data at each temperature.

of the present investigation in order to facilitate comparison at intermediate temperatures. The solid circles on the graph showing the data of Aston, Moessen, Hardy, and Szasz do not represent three separate determinations at each temperature, but result from three different methods of computing specific heats from a single series of experimental data at each temperature. The data of Templeton, Davies, and Felsing are systematically lower than those obtained in the present work, the maximum difference amounting to about 3 percent. This difference is larger than would be expected from a consideration of the estimated errors, since Templeton, Davies, and Felsing estimate their over-all accuracy as better than 1 percent.

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RESEARCH PAPER RP1641

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FREE ENERGIES AND EQUILIBRIA OF ISOMERIZATION OF THE 18 OCTANES[1]

By Edward J. Prosen, Kenneth S. Pitzer,[2] and Frederick D. Rossini

ABSTRACT

Values of the following thermodynamic properties are presented in tabular and graphical form for the 18 octanes in the ideal gaseous state, for the range 298° to 1,000°K: (a) the standard free energy of isomerization divided by the absolute temperature, $\Delta F°/T$; and (b) the relative amounts of the several isomers present in equilibrium with each other.

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I. INTRODUCTION

Values of the standard free energies of isomerization, and the corresponding equilibrium concentrations, are reported in this paper for the 18 octanes, all in the gaseous state, for the range 298° to 1,000° K. These values, similar to those previously presented for the butanes, pentanes, hexanes, and heptanes [1],[3] have been calculated from the following data:

Heats of isomerization, $\Delta H_0°$, for the normal paraffin to the branched-chain isomer given in another paper from this laboratory [2].

Entropies of all the octanes, calculated by statistical methods previously described [3, 4], which have already been published [5].

Differences in the free energy function between the normal paraffin and a given isomer, which have been claculated by the same methods and for which the values are given in table 1 for the temperatures 298°, 400°, 500°, 600°, 800°, and 1,000°K.

[1] This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection and analysis of data on the properties of hydrocarbons."

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[3] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1.—*Values of the difference in the free-energy function between n-octane and its isomers, in the gaseous state*

Compound (gas)	$\left(\frac{F^\circ-H_0^\circ}{T}\right)_{n\text{-octane}}-\left(\frac{F^\circ-H_0^\circ}{T}\right)_{\text{isomer}}$					
	298° K	400° K	500° K	600° K	800° K	1,000° K
	cal/deg mole					
n-Octane	0	0	0	0	0	0
2-Methylheptane	−0.03	−0.43	−0.70	−0.89	−1.00	−1.11
3-Methylheptane	1.81	1.35	1.01	.75	0.53	0.41
4-Methylheptane	0.11	−0.41	−0.81	−1.14	−1.44	−1.57
3-Ethylhexane	2.71	1.85	1.10	0.47	−0.23	−0.57
2,2-Dimethylhexane	−4.44	−5.06	−5.56	−5.96	−6.28	−6.38
2,3-Dimethylhexane	−1.76	−2.22	−2.55	−2.79	−2.93	−2.98
2,4-Dimethylhexane	−0.25	−1.00	−1.63	−2.11	−2.59	−2.69
2,5-Dimethylhexane	−2.17	−2.85	−3.43	−3.88	−4.39	−4.48
3,3-Dimethylhexane	−2.03	−2.85	−3.50	−3.98	−4.45	−4.54
3,4-Dimethylhexane	−3.42	−3.88	−4.28	−4.55	−4.71	−4.73
2-Methyl-3-ethylpentane	−1.94	−2.60	−3.10	−3.45	−3.72	−3.81
3-Methyl-3-ethylpentane	−3.28	−4.03	−4.67	−5.15	−5.50	−5.57
2,2,3-Trimethylpentane	−4.67	−5.51	−6.20	−6.73	−7.23	−7.41
2,2,4-Trimethylpentane	−4.67	−5.51	−6.20	−6.73	−7.23	−7.32
2,3,3-Trimethylpentane	−3.55	−4.27	−4.88	−5.34	−5.76	−5.79
2,3,4-Trimethylpentane	−3.27	−4.05	−4.72	−5.21	−5.69	−5.90
2,2,3,3-Tetramethylbutane	−11.75	−12.61	−13.27	−13.67	−13.88	−13.92

For the isomerization of the normal paraffin to the isoparaffin (normal and iso being indicated by the italic letters *n* and *i*, respectively),

$$n\text{-}C_aH_b\ (\text{gas}) = i\text{-}C_aH_b\ (\text{gas}), \tag{1}$$

ΔF° is the standard free-energy change at a given temperature, with each component in its ideal standard state of unit fugacity, and

$$\Delta\left(\frac{F^\circ-H_0^\circ}{T}\right)=\left(\frac{F^\circ-H_0^\circ}{T}\right)_i-\left(\frac{F^\circ-H_0^\circ}{T}\right)_n, \tag{2}$$

where H is the heat content, or enthalpy, and T is the absolute temperature.

But

$$\Delta\left(\frac{F^\circ-H_0^\circ}{T}\right)=\frac{\Delta F^\circ}{T}-\frac{\Delta H_0^\circ}{T} \tag{3}$$

and

$$\frac{\Delta F^\circ}{T}=-R\ln K, \tag{4}$$

where K is the equilibrium constant, as defined by Lewis and Randall [6], and R is the gas constant. Then

$$\frac{\Delta F^\circ}{T}=-R\ln K=\frac{\Delta H_0^\circ}{T}+\Delta\left(\frac{F^\circ-H_0^\circ}{T}\right). \tag{5}$$

For the isomerization reaction as given by eq 1,

$$K=f_i/f_n, \tag{6}$$

and, for low pressures,

$$K=p_i/p_n, \tag{7}$$

where f represents fugacity (see reference [6]) and p the partial pressure.

II. RESULTS IN TABULAR AND GRAPHICAL FORM

The thermodynamic quantities calculated in this way from the data referred to are given in table 2. The first two columns give the temperature in centigrade and Kelvin degrees, respectively, with the former rounded off in reference to the latter, the difference being not at all significant here. The succeeding columns give for each isomer values of the following thermodynamic properties: $\Delta F^\circ/T$, which is the standard free energy change divided by the absolute temperature for the reaction of isomerization in the gas phase, as expressed by eq 1; K, which is the equilibrium constant, defined by eq 4 and 6, for the reaction expressed by eq 1; and N, which is the mole fraction of the given isomer present at equilibrium with all of its other isomers. Strictly, the value of N so calculated is applicable only in the range from zero pressure up to that pressure at which the ratio of fugacity to pressure is still not significantly different for the several isomers. Within this range of pressure, the value of K in table 2 gives the ratio of the amount of the given isomer to the amount of the normal isomer in equilibrium with it in the gas phase. For any two other isomers, the ratio of the corresponding values of K in table 2 gives the ratio of the amounts of those two isomers present at equilibrium in the gas phase with one another.

The limits of uncertainty of the values of $\Delta F^\circ/T$ given in table 2 are estimated to be about ± 1.5 cal/deg mole.[4] This same uncertainty applies to the value of $\Delta F^\circ/T$ for the isomerization of any one of the isomers into any other one. From these values, one may easily derive the corresponding uncertainities in the values of the equilibrium constants and the equilibrium concentrations. For example, the ratio

[4] Except that the values for 2, 3-dimethylhexane may be uncertain by several times this amount [2].

TABLE 2.—*Free energies and equilibria of isomerization of the octanes*

Temperature		Octanes																	
		n-Octane			2-Methylheptane			3-Methyleptane			4-Methylheptane			3-Ethylhexane			2,2-Dimethylhexane		
t	*T*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*
°C	°K	*cal/deg mole*			*cal/deg mole*			*cal/deg mole*			*cal/deg mole*			*cal/deg mole*			*cal/deg mole*		
25	298.16	0	1	0.015	−3.63	6.21	0.091	−2.85	4.20	0.061	−0.45	1.25	0.018	−0.63	1.37	0.020	−5.29	14.3	0.21
(127)	400	0	1	.040	−2.30	3.18	.126	−2.13	2.92	.116	.16	.92	.037	−.30	1.16	.046	−2.19	3.01	.12
(227)	500	0	1	.069	−1.48	2.11	.15	−1.63	2.27	.16	.61	.74	.051	.14	0.93	.064	−0.24	1.13	.078
(327)	600	0	1	.097	−0.93	1.60	.15	−1.27	1.90	.18	.97	.61	.059	.56	.75	.073	1.13	0.57	.055
(527)	800	0	1	.13	−.36	1.20	.16	−0.92	1.59	.21	1.31	.52	.069	1.01	.60	.080	2.65	.26	.035
(727)	1000	0	1	.15	.04	0.98	.15	−.72	1.44	.22	1.47	.48	.073	1.19	.55	.084	3.48	.17	.027

Temperature		Octanes—Continued																	
		2,3-Dimethylhexane			2,4-Dimethylhexane			2,5-Dimethylhexane			3,3-Dimethylhexane			3,4-Dimethylhexane			2-Methyl-3-ethyl-pentane		
t	*T*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*
°C	°K	*cal/deg mole*			*cal/deg mole*			*cal/deg mole*			*cal/deg mole*			*cal/deg mole*			*cal/deg mole*		
25	298.16	0.32	0.85	0.012	−4.48	9.53	0.14	−5.48	15.8	0.23	−3.24	5.11	0.075	2.78	0.25	0.0036	3.18	0.20	0.0030
(127)	400	1.14	.56	.022	−2.53	3.57	.14	−2.85	4.20	.17	−1.08	1.73	.069	3.40	.18	.0072	3.53	.17	.0067
(227)	500	1.69	.43	.029	−1.19	1.82	.13	−1.13	1.77	.12	0.36	0.83	.057	3.90	.14	.0097	3.84	.15	.010
(327)	600	2.07	.35	.034	−0.24	1.12	.11	0.08	0.96	.093	1.36	.50	.049	4.23	.12	.012	4.07	.13	.013
(527)	800	2.39	.30	.040	.83	0.66	.087	1.54	.46	.061	2.49	.29	.038	4.47	.11	.014	4.18	.12	.016
(727)	1000	2.51	.28	.043	1.28	.53	.080	2.20	.33	.050	2.97	.22	.034	4.56	.10	.015	4.30	.12	.018

Temperature		Octanes—Continued																	
		3-Methyl-3-ethyl-pentane			2,2,3-Trimethylpentane			2,2,4-Trimethylpentane			2,3,3-Trimethylpentane			2,3,4-Trimethylpentane			2,2,3,3-Tetramethyl-butane		
t	*T*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*	$\Delta F°/T$	*K*	*N*
°C	°K	*cal/deg mole*			*cal/deg mole*			*cal/deg mole*			*cal/deg mole*			*cal/deg mole*			*cal/deg mole*		
25	298.16	2.11	0.35	0.0051	−0.16	1.08	0.016	−3.38	5.48	0.080	1.27	0.53	0.0077	0.62	0.73	0.011	2.49	0.29	0.0042
(127)	400	3.15	.21	.0082	1.91	0.38	.015	−0.49	1.28	.051	2.57	.27	.011	2.07	.35	.014	5.71	.057	.0023
(227)	500	3.97	.14	.0094	3.32	.19	.013	1.40	0.49	.034	3.52	.17	.012	3.14	.21	.014	7.75	.020	.0014
(327)	600	4.57	.10	.0097	4.33	.11	.011	2.73	.25	.024	4.21	.12	.012	3.89	.14	.014	9.07	.010	.0010
(527)	800	5.06	.078	.010	5.43	.065	.0086	4.23	.12	.016	4.91	.085	.011	4.70	.094	.012	10.43	.0053	.0007
(727)	1000	5.22	.072	.011	5.89	.052	.0079	4.93	.084	.013	5.11	.076	.012	5.01	.080	.012	11.16	.0036	.0006

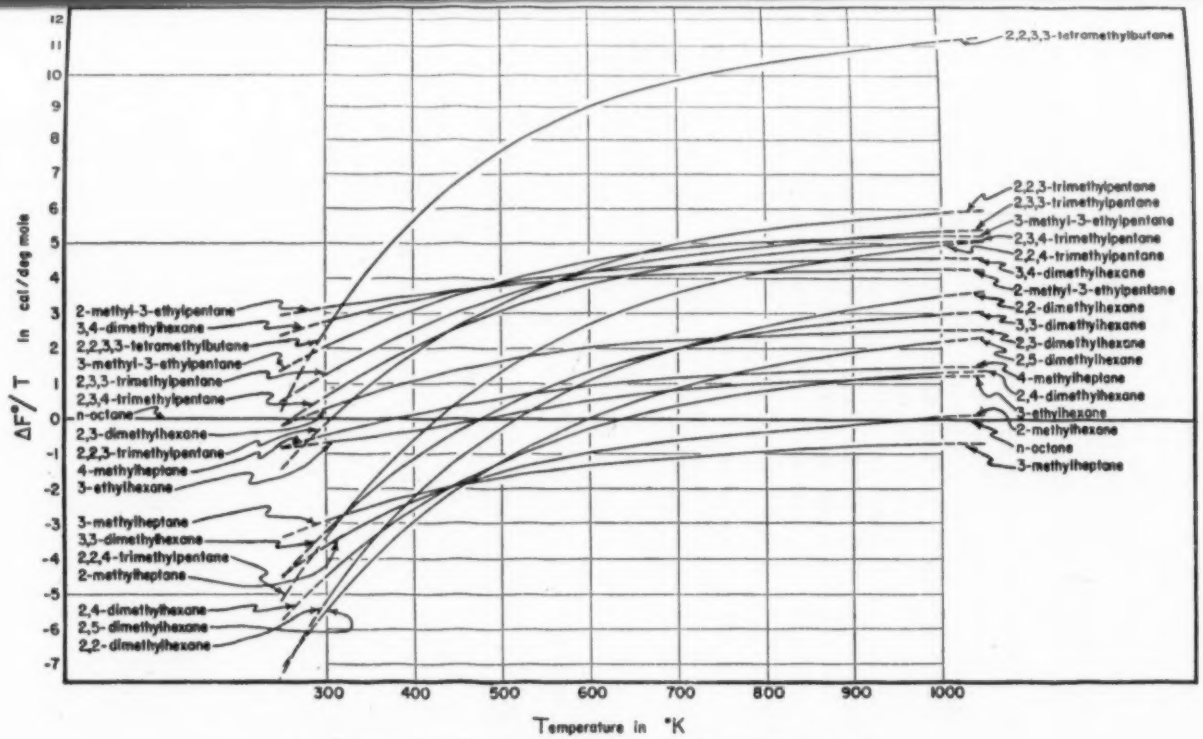

FIGURE 1.—*Free energy of isomerization of the octanes.*

The scale of ordinates gives the value of $\Delta F°/T$, in calories per degree mole, for the isomerization

$n-C_8H_{18}$ (gas) $= i-C_8H_{18}$ (gas).

The scale of abscissas gives the temperature in degrees Kelvin. For octanes having optical isomers, the values are for the racemic mixtures.

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of the values of K and N recorded in table 2 for any two given isomers may be uncertain by as much as a factor of 2. For the purpose of retaining the significance of their change with temperature, the values in table 2 are written with more figures than the foregoing uncertainties would normally warrant.

The values of $\Delta F°/T$ given in table 2 for the 18 octanes are plotted in figure 1 as a function of the temperature. From this chart, one may see at a glance, for any temperature in the given range and within the limits of uncertainty of the present calculations, which of the isomers is thermodynamically the most stable (lowest value of $\Delta F°/T$), which is the least stable (highest value of $\Delta F°/T$), and the order of stability of the other isomers. From the preceding discussion regarding uncertainties, it follows that those isomers having at some given temperature values of $\Delta F°/T$ that differ by less than the uncertainty are those for which the exact order of stability cannot be stated, since the values overlap. In such cases, the amounts present at equilibrium will be equal, within the given limits.

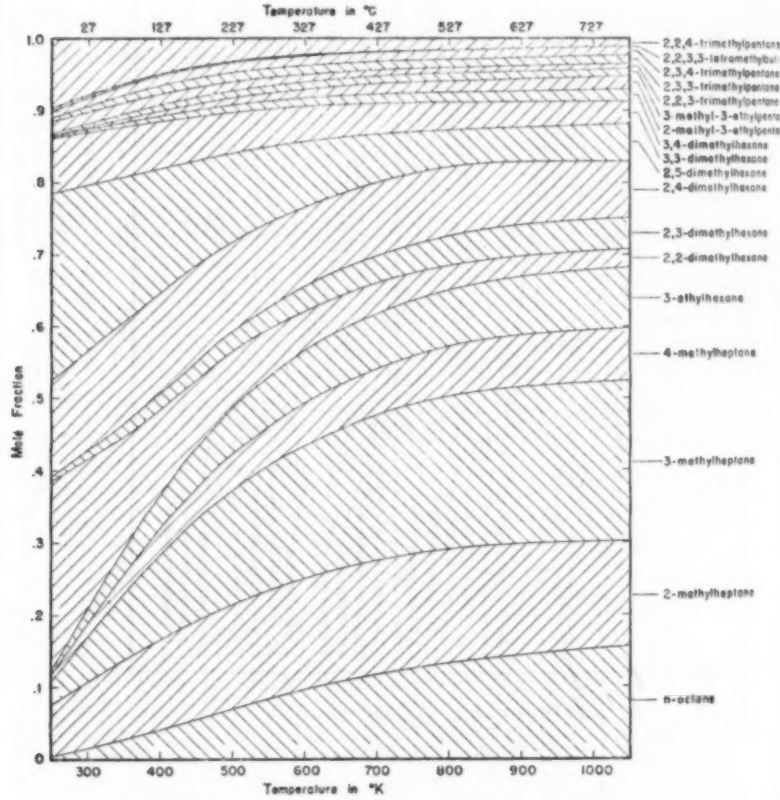

FIGURE 2.—*Equilibrium concentrations of the octanes.*

The scale of ordinates measures the amount, in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

In figure 2 are plotted, as a function of the temperature, the amounts, in mole fraction, of each of the isomers present at equilibrium with all its other isomers in the gas phase, as given in table 2. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures.

III. DISCUSSION

The values presented in this report for the octanes follow substantially the general conclusions previously drawn for the butanes, pentanes, hexanes, and heptanes, with regard to thermodynamic stability in the gaseous state:

(a) At 25° C, the normal isomer is among the isomers of lesser stability. Relative to the other isomers, the normal isomer increases in stability with increase in temperature, and at 1,000° K is among the most stable of the isomers.

(b) At 25° C, 2,2-dimethylhexane is among the most stable of the isomers, but it rapidly becomes less stable with increasing temperature and at 1,000° K is among the least stable of the isomers.

(c) The more highly branched isomers are among the least stable at the higher temperatures.

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HEATS OF COMBUSTION AND FORMATION OF THE PARAFFIN HYDROCARBONS AT 25 C [1]

By Edward J. Prosen and Frederick D. Rossini

ABSTRACT

Selected "best" values are given for the heats of combustion (in oxygen to form gaseous carbon dioxide and liquid water) and the heats of formation (from the elements solid carbon, graphite, and gaseous hydrogen) for methane and ethane in the gaseous state, and for all the paraffin hydrocarbons from propane through the octanes and the normal paraffins through eicosane, in both the liquid (except for one octane which is solid) and gaseous states, all at 25° C. Equations are given for calculating values for all the normal paraffins above eicosane.

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I. INTRODUCTION

In 1940, values were presented by this Bureau for the heats of formation of the paraffin hydrocarbons from methane through the pentanes, in the gaseous state [1].[2] Since then, a considerable amount of new data has become available, which makes possible the extension of these values to all the isomers of the hexanes, heptanes, and octanes, and to the higher normal paraffins, each in both the liquid and gaseous states. In arriving at the new values given in this paper, cognizance was also taken of slight revisions that have been made in the values of the heats of formation of carbon dioxide and water. This paper also gives values for the increment in energy per CH_2 group for the normal paraffins beyond pentane, for both the heat of combustion and the heat of formation, in both the liquid and gaseous states.

[1] This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection and Analysis of Data on the Properties of Hydrocarbon."

[2] Figures in brackets indicate the literature references at the end of the paper.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the values presented in this paper are based is the international joule determined by standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau. Conversion to the conventional thermochemical calorie is made by means of the relation [16]:

4.1833 international joules (NBS)=1 calorie.

The atomic weights of hydrogen, oxygen, and carbon were taken as 1.0080, 16.0000, and 12.010, respectively, from the 1941 table of International Atomic Weights [17].

The uncertainties assigned to the various quantities dealt with were derived, where possible, by a method previously described [18]. In other cases, reasonable estimates of the uncertainty were made.

III. EXPERIMENTAL DATA CONSIDERED

In arriving at the selected values presented in this paper, consideration was given to experimental values for the following:

Heats of combustion of methane, ethane, propane, *n*-butane, isobutane, and *n*-pentane, each in the gaseous state, by Rossini [1, 2, 3, 24].

Heats of combustion of isopentane and neopentane (tetramethylmethane), in the gaseous state, by Knowlton and Rossini [1, 4].

Heats of combustion of *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, and *n*-dodecane, in the liquid state, by Jessup [5].

Heats of combustion of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, and *n*-hexadecane, in the liquid state, by Prosen and Rossini [6].

Heats of isomerization of the five hexanes, in the liquid state, by Prosen and Rossini [7].

Heats of isomerization of the nine heptanes, in the liquid state, by Prosen and Rossini [8].

Heats of isomerization of the 18 octanes, in the liquid state, by Prosen and Rossini [9].

Standard heats of vaporization at 25° C for the 3 pentanes, 5 hexanes, 9 heptanes, 18 octanes, and the higher normal paraffins, from a correlation by Wagman, Taylor, and Rossini [10] of selected "best" values based largely on the experimental data on the heats of vaporization of *n*-pentane, 5 hexanes, 7 heptanes, 18 octanes, *n*-nonane and *n*-decane, at 25° C, by Osborne and Ginnings [11].

Heat of formation of carbon dioxide, by Prosen, Jessup, and Rossini [12], which is a revision of the previously selected "best" value, by Rossini and Jessup [13].

Heat of formation of water, by Rossini, et. al. [14], which is a slight revision of the previously selected "best" value by Rossini [15].

Consideration of earlier data on the heats of combustion of the paraffin hydrocarbons has already been made [2, 3, 4, 5, 7, 8, 9], except for measurements on *n*-hexadecane by Richardson and Parks [25]. Corrected to the same unit of energy, their value for *n*-hexadecane

differs from that of Prosen and Rossini [6] by -0.025 ± 0.032 percent.

A summary of the NBS data on the heats of combustion of the normal paraffin hydrocarbons is given in table 1, in which the values represent the decrement in heat content for the reaction

$$C_nH_{2n+2}\ (\text{gas}) + \frac{3n+1}{2}\ O_2\ (\text{gas}) = nCO_2\ (\text{gas}) + (n+1)H_2O\ (\text{liq})$$

as deduced from several investigations made at this Bureau within the past 15 years. Where appropriate, data obtained for the liquid hydrocarbon have been converted to the gaseous state with selected values of the standard heat of vaporization at 25° C [10, 11].

TABLE 1.—*Summary of the NBS data on the heats of combustion of the normal paraffin hydrocarbons*

Compound	Value of the heat of combustion at 25°C, $-\Delta Hc°_{298.16}$, of the gaseous hydrocarbon, to form gaseous carbon dioxide and liquid water, from the data of—		
	[1, 2, 3]	[5]	[6]
	kcal/mole	*kcal/mole*	*kcal/mole*
Methane	212.798 ±0.072	----------	----------
Ethane	372.820 ±0.110	----------	----------
Propane	530.605 ±0.133	----------	----------
n-Butane	687.982 ±0.167	----------	----------
n-Pentane	845.30 ±0.22	----------	845.07 ±0.18
n-Hexane	----------	1002.72 ±0.33	1002.55 ±0.20
n-Heptane	----------	1159.89 ±0.45	1160.07 ±0.21
n-Octane	----------	1317.30 ±0.34	1317.46 ±0.25
n-Nonane	----------	1474.77 ±0.45	1474.99 ±0.27
n-Decane	----------	1632.31 ±0.27	1632.41 ±0.36
n-Undecane	----------	1789.59 ±0.61	----------
n-Dodecane	----------	1947.86 ±0.75	1947.37 ±0.39
n-Hexadecane	----------	----------	2576.97 ±0.68

The values deduced from references [2, 3] are the same as reported indirectly in reference [1], with a small correction for the molecular weight of water (since in these experiments, the mass of water formed in the combustion was used to determine the amount of reaction) and also with a slight change in conversion to zero pressure.

The values deduced from reference [5] were obtained as a result of the following corrections, in addition to the conversion to the gaseous state: (a) a change in the energy equivalent of the calorimeter system and in the correction for the formation of nitric acid, made by Jessup [19] in accordance with the procedure described on page 262 of reference [20]; (b) a change in the reference states of the gaseous reactants and products to the thermodynamic standard state of unit fugacity (in which the energy content is the same as that of the real real gas at zero pressure); (c) a change in the amount of reaction, the number of moles of hydrocarbon burned being taken as equal to 0.99965 ± 0.00010 times the mass of the sample divided by the molecular weight of the given hydrocarbon. The factor 0.99965 is the average obtained in the experiments on the same compounds described in reference [6], and was there determined as the ratio of the mass of carbon dioxide formed in the combustion to the mass of carbon dioxide calculated stoichiometrically from the mass of the

sample. In connection with the data from reference [5], it may be pointed out that the purities of the normal paraffin hydrocarbons measured in that investigation were lower than of the corresponding compounds described in reference [6] by amounts ranging from zero to 0.9 mole percent, as calculated from the freezing points [21] of the compounds measured in reference [5] and the freezing point for zero impurity [22].

The values attributed to reference [6] are the same as those given in that report, with conversion being made to the gaseous state, as previously described.

IV. SELECTED VALUES

In table 2 are given the selected "best" values for the heats of combustion and formation of methane and ethane in the gaseous state, and of propane, the 2 butanes, the 3 pentanes, the 5 hexanes, the 9 heptanes, the 18 octanes, and all the higher normal paraffins, in both the liquid and gaseous states. Equations are given for calculating values for all the normal paraffins above eicosane.

The values of heats of combustion given in table 2 for methane, ethane, propane, and *n*-butane, in the gaseous state, are the same as in table 1. The value for gaseous *n*-pentane is taken as the weighted mean of the values from [3] and [6]. The corresponding values for the liquid state were obtained by applying the standard heat of vaporization.

The values for the normal paraffins above pentane were obtained by fitting an equation linear in the number of carbon atoms to the data in table 1 [23]. By the method of least squares, using the data for the normal paraffins from hexane to dodecane, inclusive, and weighting the values inversely as the squares of their assigned uncertainties, the following equation was obtained for the relation between the number of carbon atoms in the molecule and the heat of combustion of the gaseous hydrocarbon at 25° C:

$$C_nH_{2n+2}(\text{gas})+\frac{3n+1}{2}O_2(\text{gas})=nCO_2(\text{gas})+(n+1)H_2O(\text{liq}) \quad (1)$$

$$-\Delta Hc^\circ{}_{298\cdot16}=57.909+157.443n\pm(0.1647-0.03902n+0.002684n^2)^{1/2} \text{ kcal/mole; } n>5. \quad (2)$$

The uncertainties attached to the constants in eq 2 represent the over-all uncertainties insofar as they can be estimated [18].

The corresponding equations representing the heat of combustion of the liquid hydrocarbon at 25° C, and applicable to the normal paraffins above pentane, is

$$C_nH_{2n+2}(\text{liq})+\frac{3n+1}{2}O_2(\text{gas})=nCO_2(\text{gas})+(n+1)H_2O(\text{liq}) \quad (3)$$

$$-\Delta Hc^\circ{}_{298\cdot16}=57.430+156.263n\pm(0.1653-0.03916n+0.002694n^2)^{1/2} \text{ kcal/mole; } n>5. \quad (4)$$

TABLE 2.—*Selected "best" values for the heats of combustion and formation of the paraffin hydrocarbons*

Compound	Formula	Heat of combustion [a] at 25° C, $-\Delta Hc^\circ$		Heat of formation [b] at 25° C, ΔHf°	
		Liquid	Gas	Liquid	Gas
		kcal/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*
Methane	CH_4		212.798±0.072		−17.889±0.075
Ethane	C_2H_6		372.820±0.110		−20.236±0.116
Propane	C_3H_8	526.782[c] ±0.133	530.605±0.133	−28.643[c] ±0.142	−24.820±0.142
n-Butane	C_4H_{10}	682.844[c] ±0.167	687.982±0.167	−34.950[c] ±0.179	−29.812±0.179
2-Methylpropane	C_4H_{10}	681.625[c] ±0.151	686.342±0.151	−36.169[c] ±0.164	−31.452±0.164
n-Pentane	C_5H_{12}	838.80 ±0.14	845.16 ±0.14	−41.36 ±0.16	−35.00 ±0.16
2-Methylbutane	C_5H_{12}	837.30 ±0.18	843.24 ±0.18	−42.86 ±0.20	−36.92 ±0.20
2,2-Dimethylpropane	C_5H_{12}	835.18[c]±0.24	840.49 ±0.24	−44.98[c]±0.25	−39.67 ±0.25
n-Hexane	C_6H_{14}	995.01 ±0.17	1002.57 ±0.17	−47.52 ±0.19	−39.96 ±0.19
2-Methylpentane	C_6H_{14}	993.71 ±0.23	1000.87 ±0.23	−48.82 ±0.25	−41.66 ±0.25
3-Methylpentane	C_6H_{14}	994.25 ±0.21	1001.51 ±0.21	−48.28 ±0.23	−41.02 ±0.23
2,2-Dimethylbutane	C_6H_{14}	991.52 ±0.21	998.18 ±0.21	−51.01 ±0.23	−44.35 ±0.23
2,3-Dimethylbutane	C_6H_{14}	993.05 ±0.22	1000.04 ±0.22	−49.48 ±0.24	−42.49 ±0.24
n-Heptane	C_7H_{16}	1151.27 ±0.15	1160.01 ±0.15	−53.63 ±0.19	−44.89 ±0.19
2-Methylhexane	C_7H_{16}	1149.97 ±0.28	1158.30 ±0.28	−54.93 ±0.30	−46.60 ±0.30
3-Methylhexane	C_7H_{16}	1150.55 ±0.28	1158.94 ±0.28	−54.35 ±0.30	−45.96 ±0.30
3-Ethylpentane	C_7H_{16}	1151.13 ±0.26	1159.56 ±0.26	−53.77 ±0.28	−45.34 ±0.28
2,2-Dimethylpentane	C_7H_{16}	1147.85 ±0.30	1155.61 ±0.30	−57.05 ±0.32	−49.29 ±0.32
2,3-Dimethylpentane	C_7H_{16}	1149.09 ±0.28	1157.28 ±0.28	−55.81 ±0.30	−47.62 ±0.30
2,4-Dimethylpentane	C_7H_{16}	1148.73 ±0.20	1156.60 ±0.20	−56.17 ±0.23	−48.30 ±0.23
3,3-Dimethylpentane	C_7H_{16}	1148.83 ±0.19	1156.73 ±0.19	−56.07 ±0.22	−48.17 ±0.22
2,2,3-Trimethylbutane	C_7H_{16}	1148.27 ±0.25	1155.94 ±0.25	−56.63 ±0.27	−48.96 ±0.27
n-Octane	C_8H_{18}	1307.53 ±0.16	1317.45 ±0.16	−59.74 ±0.20	−49.82 ±0.20
2-Methylheptane	C_8H_{18}	1306.28 ±0.28	1315.77 ±0.28	−60.99 ±0.31	−51.50 ±0.31
3-Methylheptane	C_8H_{18}	1306.92 ±0.24	1316.45 ±0.24	−60.35 ±0.27	−50.82 ±0.27
4-Methylheptane	C_8H_{18}	1307.09 ±0.25	1316.58 ±0.25	−60.18 ±0.28	−50.69 ±0.28
3-Ethylhexane	C_8H_{18}	1307.39 ±0.23	1316.87 ±0.23	−59.88 ±0.26	−50.40 ±0.26
2,2-Dimethylhexane	C_8H_{18}	1304.64 ±0.21	1313.56 ±0.21	−62.63 ±0.24	−53.71 ±0.24
2,3-Dimethylhexane	C_8H_{18}	1306.86 ±0.34	1316.14 ±0.34	−60.41 ±0.36	−51.13 ±0.36
2,4-Dimethylhexane	C_8H_{18}	1305.80 ±0.24	1314.83 ±0.24	−61.47 ±0.27	−52.44 ±0.27
2,5-Dimethylhexane	C_8H_{18}	1305.00 ±0.34	1314.06 ±0.34	−62.27 ±0.36	−53.21 ±0.36
3,3-Dimethylhexane	C_8H_{18}	1305.68 ±0.23	1314.66 ±0.23	−61.59 ±0.26	−52.61 ±0.26
3,4-Dimethylhexane	C_8H_{18}	1307.04 ±0.35	1316.36 ±0.35	−60.23 ±0.37	−50.91 ±0.37
3-Methyl-3-ethylpentane	C_8H_{18}	1307.58 ±0.28	1316.79 ±0.28	−59.69 ±0.31	−50.48 ±0.31
3-Methyl-3-ethylpentane	C_8H_{18}	1306.80 ±0.27	1315.89 ±0.27	−60.47 ±0.30	−51.38 ±0.30
2,2,3-Trimethylpentane	C_8H_{18}	1305.83 ±0.34	1314.66 ±0.34	−61.44 ±0.36	−52.61 ±0.36
2,2,4-Trimethylpentane	C_8H_{18}	1305.29 ±0.30	1313.70 ±0.30	−61.98 ±0.32	−53.57 ±0.32
2,3,3-Trimethylpentane	C_8H_{18}	1306.64 ±0.31	1315.54 ±0.31	−60.63 ±0.33	−51.73 ±0.33
2,3,4-Trimethylpentane	C_8H_{18}	1306.28 ±0.38	1315.30 ±0.38	−60.99 ±0.40	−51.97 ±0.40
2,2,3,3-Tetramethylbutane	C_8H_{18}	1303.03[d]±0.44	1313.28 ±0.44	−64.24[d]±0.46	−53.99 ±0.46
n-Nonane	C_9H_{20}	1463.80 ±0.18	1474.90 ±0.18	−65.84 ±0.22	−54.74 ±0.22
n-Decane	$C_{10}H_{22}$	1620.06 ±0.21	1632.34 ±0.21	−71.95 ±0.26	−59.67 ±0.26
n-Undecane	$C_{11}H_{24}$	1776.32 ±0.25	1789.78 ±0.25	−78.06 ±0.30	−64.60 ±0.30
n-Dodecane	$C_{12}H_{26}$	1932.59 ±0.29	1947.23 ±0.29	−84.16 ±0.34	−69.52 ±0.34
n-Tridecane	$C_{13}H_{28}$	2088.85 ±0.33	2104.67 ±0.33	−90.27 ±0.39	−74.45 ±0.39
n-Tetradecane	$C_{14}H_{30}$	2245.11 ±0.38	2262.11 ±0.38	−96.38 ±0.43	−79.38 ±0.43
n-Pentadecane	$C_{15}H_{32}$	2401.37 ±0.43	2419.55 ±0.43	−102.49 ±0.48	−84.31 ±0.48
n-Hexadecane	$C_{16}H_{34}$	2557.64 ±0.48	2577.00 ±0.48	−108.59 ±0.53	−89.23 ±0.53
n-Heptadecane	$C_{17}H_{36}$	2713.90 ±0.53	2734.44 ±0.53	−114.69 ±0.58	−94.15 ±0.58
n-Octadecane	$C_{18}H_{38}$	2870.16 ±0.58	2891.88 ±0.58	−120.80 ±0.64	−99.08 ±0.64
n-Nonadecane	$C_{19}H_{40}$	3026.43 ±0.63	3049.33 ±0.63	−126.90 ±0.69	−104.00 ±0.69
n-Eicosane	$C_{20}H_{42}$	3182.69 ±0.68	3206.77 ±0.68	−133.01 ±0.74	−108.93 ±0.74
per CH_2		156.263	157.443	−6.106	−4.926

[a] $-\Delta Hc^\circ_{298.16}$ represents the heat evolved in the combustion of the given hydrocarbon in the state indicated, in gaseous oxygen to form gaseous carbon dioxide and liquid water, at 25° C and constant pressure, with all reactants and products in their appropriate standard reference states, unless otherwise indicated.

[b] $\Delta Hf^\circ_{298.16}$ represents the increment in the heat content of the process of forming the given hydrocarbon in the state indicated, from its elements, at 25° C, with all reactants and products in their appropriate standard reference states, unless otherwise indicated.

[c] At saturation pressure.

[d] For the solid state.

Similarly, the heats of formation of the normal paraffins above pentane, for the gaseous state at 25° C, are given by the equations

$$n\mathrm{C}(c, \text{graphite}) + (n+1)\mathrm{H_2}(\text{gas}) = \mathrm{C}_n\mathrm{H}_{2n+2}(\text{gas}) \quad (5)$$

$$\Delta Hf^\circ_{298.16} = -10.408 - 4.926n \pm (0.1648 - 0.03884n + 0.002893n^2)^{1/2} \text{ kcal/mole; } n > 5. \quad (6)$$

The corresponding equations for the formation of the normal paraffins above pentane in the liquid state at 25° C are

$$n\mathrm{C}(c, \text{graphite}) + (n+1)\mathrm{H_2}(\text{gas}) = \mathrm{C}_n\mathrm{H}_{2n+2}(\text{liq}) \quad (7)$$

$$\Delta Hf^\circ_{298.16} = -10.887 - 6.106n \pm (0.1654 - 0.03898n + 0.002903n^2)^{1/2} \text{ kcal/mole; } n > 5. \quad (8)$$

The values given in table 2 for the heats of combustion of the normal paraffins above pentane were calculated from eq 2 and 4, and the values for the heats of formation of the same compounds were calculated from eq 6 to 8.

The values for isobutane, 2-methylbutane (isopentane), and 2,2-dimethylpropane (neopentane), in the gaseous state, were calculated, using the heats of isomerization from the appropriate normal paraffin hydrocarbon given in reference [1]. The corresponding values for the liquid state were obtained by applying the heat of vaporization [10].

The values for the 4 branched-chain hexanes, the 8 branched-chain heptanes, and the 17 branched-chain octanes, in the liquid state for all except 1 octane, which is solid at 25° C, were calculated, using the heats of isomerization from the appropriate normal paraffin hydrocarbon given in references [7, 8, 9]. The corresponding values for the gaseous state were obtained by applying the heats of vaporization [10].

The over-all uncertainties on many of the values given in table 2 have arbitrarily been made somewhat larger than would be calculated from the known uncertainties of the components of the calculation.

The values for the heats of combustion and formation of all the paraffin hydrocarbons through the octanes presented in table 2, which are based on experimental measurements, are being utilized to estimate the corresponding values for the 34 branched-chain nonanes, the 74 branched-chain decanes, etc. Deviations from linearity for the normal paraffins below pentane will be discussed in a later report covering several homologous series.

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COMPARISON OF THE PURITY OF SAMPLES OF ORGANIC SOLVENTS BY ULTRAVIOLET SPECTROPHOTOMETRY

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ABSTRACT

Studies of the uniformity of different samples of organic solvents by ultraviolet spectrophotometry are described. The procedure used is applicable to the detection of impurities originally present or formed by deterioration and to the study of the effectiveness of purification procedures.

Absorption curves are given for *n*-heptane, 2,2,4-trimethylpentane, cyclohexane, methylcyclohexane, decahydronaphthalene, benzene, carbon tetrachloride, methyl alcohol, ethyl alcohol, ethyl acetate, and dioxane, in two or more grades of purity. The absorption curves of tetrahydronaphthalene, toluene, xylene, chlorobenzene, ethylene dichloride, trichloroethylene, acetone, dimethyldioxane, and carbon bisulfide are discussed briefly. The effect of filtration through silica gel on the ultraviolet absorption of several commercial solvents is shown.

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I. INTRODUCTION

In spectrophotometric studies performed as part of a research project for the development of indicators for acidity and basicity in hydrocarbons and certain other organic solvents, it was necessary to remove impurities from the solvents and to determine their ultraviolet transmittancy. The absorption curves of samples of a given solvent from various sources or in successive stages of purification showed significant and sometimes striking differences. Similar comparisons were then made of various samples of additional types of solvents. The results showed that ultraviolet spectrophotometry is widely applicable as a criterion of uniformity of different specimens

of a given solvent and is sometimes a more sensitive method than determinations of density, refractive index, or other physical properties. This should not be surprising in view of the fact that a large number of the organic solvents in common use may contain impurities which show intense spectral absorption, even in concentrations of the order of 10^{-5} M or less.

A few examples of the use of ultraviolet spectrography or spectrophotometry in the examination of organic solvents have been published [1 to 6].[1] [2] However, a general application of ultraviolet spectrophotometry to the study of impurities in organic solvents has not been reported. Inasmuch as ultraviolet spectrophotometers are increasingly accessible to laboratory workers, the purpose of the present paper is to direct attention to possible advantages of using such equipment for the qualitative detection of highly absorbing impurities and in some cases for their quantitative estimation. As the reproductibility obtained with the equipment under controlled conditions is 0.1 to 0.2 percent, the spectrophotometric method is more precise, rapid, and convenient than spectrography for such work.

This paper describes the procedure used in obtaining the absorption-curves and shows its application to detecting the presence of impurities in the original solvent or the formation of impurities by deterioration of the solvent after purification, as well as to studying the relative efficiencies of different methods of purification.[3] It may also be used in the selection of spectral cutoff filters for various regions in the ultraviolet [7, 8, 15, 16].

II. APPARATUS AND METHOD

A Beckman quartz photoelectric spectrophotometer[4] was modified by replacing the cell compartment with a light-tight box having a slide for holding two 38-mm (inside diameter) cylindrical metal cell holders in which stoppered quartz cylinders 1 cm in length were fitted with matched crystalline quartz end plates to hold the solutions. One cell was filled with distilled water and the other with the solvent under investigation. The transmittancy of the cell containing distilled water was taken as 100 percent at each wavelength. Measurements were performed at 26° ±2° C. Readings were recorded at 5-mμ intervals from 200 mμ to the wavelength at which the organic solvent showed 100-percent transmission.[5] The reproducibility of the transmittancy values was usually within ±0.2 percent, except at the lowest wavelengths (200 to 230 mμ) where there occur greater deviations, usually of the order of ±0.5 percent and occasionally larger, and where an apparent increase in transmittancy (see also fig. 3, A) may be due to scattered light.

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] According to a private communication the quartz spectrophotometer is being used for the determination of benzene and toluene in mixtures of paraffins and naphthenes.

[3] Contamination of the solvent by an improperly chosen container, stopper, or cap interliner can likewise be detected by this method.

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[5] In a few experiments with impure solvents, for example, methyl alcohol, figure 5A, it was not considered worthwhile to complete the measurements to 100-percent transmission.

III. DATA AND DISCUSSION

The data are represented graphically in figures 1 to 6, in which transmittancy, in percent, is plotted with respect to wavelength in millimicrons. Circles shown on the curves represent experimental points. To avoid confusion some points were omitted in the graphs.

1. PARAFFIN AND CYCLOPARAFFIN HYDROCARBONS

Unsaturated or aromatic impurities are frequently present in saturated hydrocarbon solvents. Filtration of the solvent through various adsorbents is very effective for the removal of such impurities. Silica gel is a particularly efficient adsorbent that has been used extensively for removing aromatic and unsaturated compounds in the purification of petroleum hydrocarbons [9, 10, 11]. The number of filtrations required depends upon the type and amount of impurity, as well as upon the relative amounts of solvent and adsorbent. The effects produced by silica gel treatment [9] on the absorption curves of commercial *n*-heptane, cyclohexane, methylcyclohexane, 2,2,4-trimethylpentane, and decahydronaphthalene are shown in figures 1 to 3.

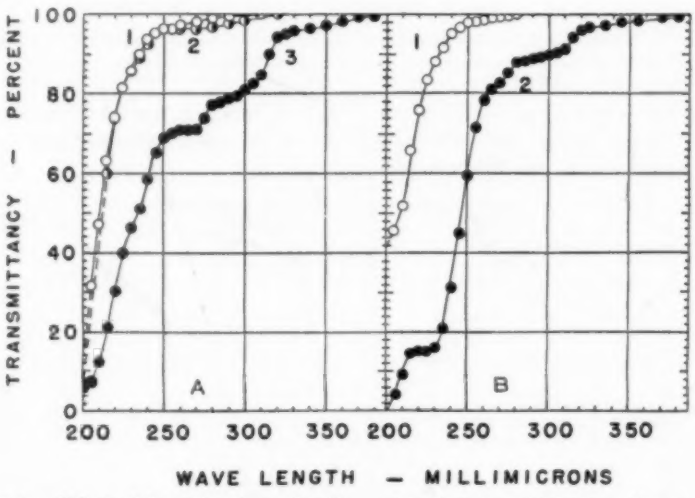

FIGURE 1.—*Effect of filtration through silica gel on the ultraviolet absorption spectrum of commercial* n*-heptane.*

A, Sample *X*. 1, after three filtrations; 2, after one filtration; 3, original material.
B, Sample *Y*. 1, after one filtration; 2, original material.

n-*Heptane.*—In figure 1, A, curves 3, 2, and 1 represent, respectively, the original solvent (from source *X*) and the products obtained by one and three filtrations. Apparently the major portion of the impurity was removed by the first filtration. In figure 1, B, curves 2 and 1 correspond, respectively, to the original *n*-heptane (from source *Y*) and the product from one filtration. No further change was observed after a second filtration.

Cyclohexane.—Figure 2, A, shows the absorption curves for commercial solvent (curve 2) and for the product obtained by filtration through silica gel to constant density (curve 1).[6]

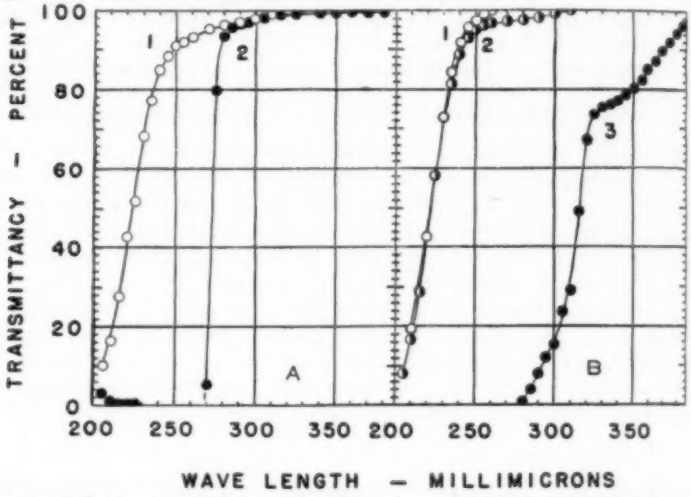

FIGURE 2.—*Effect of filtration through silica gel on the ultraviolet absorption spectrum.*
A, Commercial cyclohexane. 1, after filtrations giving constant density; 2, original material.
B, Commercial methylcyclohexane. 1, after four filtrations; 2, after one filtration; 3, original material.

Methylcyclohexane.—In figure 2, B, curves 3, 2, and 1 were obtained, respectively, with commercial solvent and the products from one and from four silica gel filtrations.

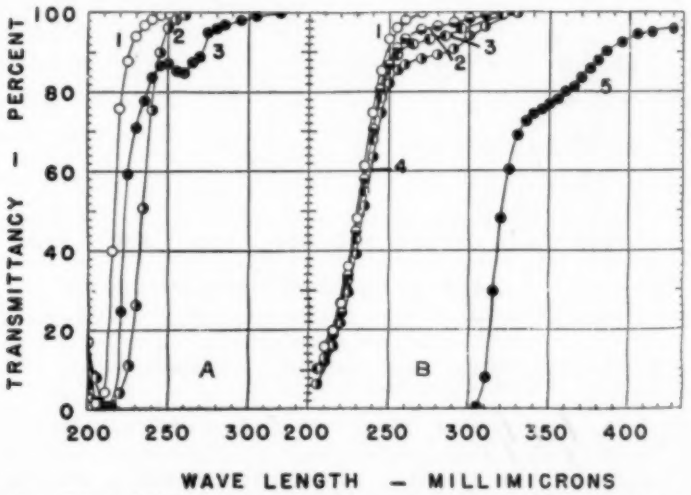

FIGURE 3.—*Effect of filtration through silica gel on the ultraviolet-absorption spectrum.*
A, Commercial high-grade 2, 2, 4-trimethylpentane. 1, after two filtrations; 2, after one filtration; 3, original material.
B, Commercial decahydronaphthalene. 1, after five filtrations; 2, after three filtrations; 3, after two filtrations; 4, after one filtration; 5, original material.

[6] The original cyclohexane had the refractive index, n_D^{25}, 1.4246 (Abbe refractometer) and specific gravity d^{25}, 0.77830. The final constants obtained were n_D^{25}, 1.4230 and d^{25}, 0.77580. These values were determined by Elizabeth Murray Gilsey.

2,2,4-Trimethylpentane[7].—In figure 3, A, absorption curves 3, 2, and 1 correspond, respectively, to a commercial high grade of solvent and to the products from one and from two silica gel filtrations. A third filtration did not produce further measurable change. The greater absorption in the region below 245 mμ produced by one filtration of the solvent through silica gel seems anomalous (compare curves 3 and 2). Insufficient material was available to check these results. The only evident source of contamination was a possible indirect introduction of impurities by a refluxing action of the solvent at room temperature upon a rubber connection. The use of all-glass apparatus for such materials is recommended. The most plausible alternative explanation is a cracking action of silica gel upon some impurity or impurities in the solvent during the first filtration.

Decahydronaphthalene.—Curves 5, 4, 3, 2, and 1 in figure 3,B, were obtained with commercial solvent and the products from, respectively, 1, 2, 3, and 5 silica gel filtrations. In the region 250 to 270 mμ, the fifth filtration increased the transmittancy about 1 percent above that observed after 4 filtrations.

2. AROMATIC HYDROCARBONS

Benzene.—In figure 4, A, curves 3, 2, and 1 were obtained with three grades of solvent: a technical grade,[8] a commercial high grade,[9] and

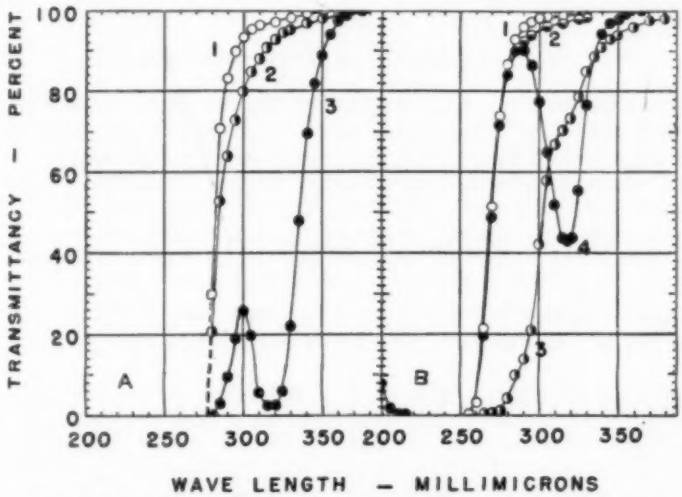

FIGURE 4.—*Ultraviolet-absorption spectra of different specimens.*

A, Commercial benzene. 1, high-grade benzene after purification; 2, the same, before purification; 3, technical-grade benzene.

B, Commercial carbon tetrachloride. 1 and 3, samples stated to meet ACS specifications; 2, "sulphur-free" grade; 4, technical grade.

the product obtained by drying the high-grade benzene for several days over Drierite and redistilling. Curve 1 was also obtained from

[7] Said by the manufacturer to be 99.7 percent pure and to contain only isomeric octanes.

[8] The technical grade of benzene possessed an odor that suggested the presence of carbon bisulfide and gave positive reactions in the Liebermann-Seyewetz [12] and Pierce [13] tests for this substance, as well as a negative test for thiophene [14].

[9] The commercial high-grade benzene gave negative tests for carbon bisulfide and thiophene.

benzene purified by a second method, which involved shaking the benzene several times with fresh portions of concentrated sulfuric acid, allowing it to stand for some time over the acid, separating the two layers, washing, drying, and distilling. Since differences in the absorption curves of samples of benzene purified by these two methods might be observed in the region below 280 mμ if shorter absorption cells were used, the studies are to be extended to the use of 5-mm and 1-mm cells.

After approximately 20 ml of the purified benzene was stirred with a rod that had been dipped in carbon bisulfide, a narrow absorption band was obtained near 320 mμ and the transmittancy at 320 mμ was reduced nearly 25 percent. The similar absorption band in curve 3 was, therefore, probably due to the presence of carbon bisulfide in the technical grade of benzene. The magnitude of the absorption index at 320 mμ is therefore suggested as a possible quantitative measure of carbon bisulfide.

Homologs of benzene.—Comparative absorption curves for benzene, toluene, and xylene showed no inflections, but a gradual displacement toward the visible with increasing molecular weight of the solvent.

Tetrahydronaphthalene.—A commercial grade of the solvent gave no measurable transmission below 325 mμ and showed gradually diminishing absorption to 550 mμ. There seemed to be a very slight shoulder in the region below 350 mμ.

3. CHLORINATED HYDROCARBONS

Carbon tetrachloride.—Absorption curves for four commercial grades of the solvent are given in figure 4, B. Curves 1 and 3 were obtained with products labeled as complying with ACS specifications. Curves 4 and 2 were obtained, respectively, with a technical grade and a grade labeled "sulfur-free." The absorption band near 320 mμ obtained with a technical grade of carbon tetrachloride, as well as with a technical grade of benzene (fig. 4, A), was probably due to carbon bisulfide. One filtration of the technical carbon tetrachloride through silica gel was found to increase the transmittancy at 320 mμ more than 12 percent and the transmittancy at 290 mμ nearly 5 percent.

Ethylene dichloride.—Commercial products from two sources, *X* and *Y*, showed a band in the region 225 mμ and a "shoulder" in the region 265 to 285 mμ, but sample *Y* absorbed more light than sample *X* (e. g., 7.4 percent more at 275 mμ). Absorption by sample *X* diminished slightly (1.7 percent at 275 mμ) after it had been allowed to stand in a colorless bottle for some time.

Chlorobenzene.—Simple distillation of a commercial high grade of the solvent produced a marked change in the spectrum (e. g., 25.3 percent higher transmittancy at 300 mμ). The solvent gave no measurable transmission below 285 mμ.

Trichloroethylene.—The absorption curve of a technical grade shifted appreciably toward the ultraviolet after the solvent was washed with dilute alkali and water, dried, and distilled. The unpurified solvent showed no measurable transmission up to 300 mμ and complete

transmission at 620 mμ, but the purified solvent transmitted completely at 410 mμ and showed a shallow absorption band near 320 mμ and evidence of a second absorption band near 250 mμ.

4. COMPOUNDS CONTAINING OXYGEN

Methyl alcohol.—Curves 1, 2, and 3 in figure 5, A, were obtained with three different specimens of this solvent, all supposedly of high grade. Sample *X*, which gave curve 1, was said to be synthetic methyl alcohol. The history of sample *Y*, which gave curve 2, is not known. Curve 3 was obtained from methyl alcohol that had been prepared a year previously by two distillations of a commercial grade (sample Z, probably not synthetic) from magnesium. Deterioration of the sample upon standing may have occurred.

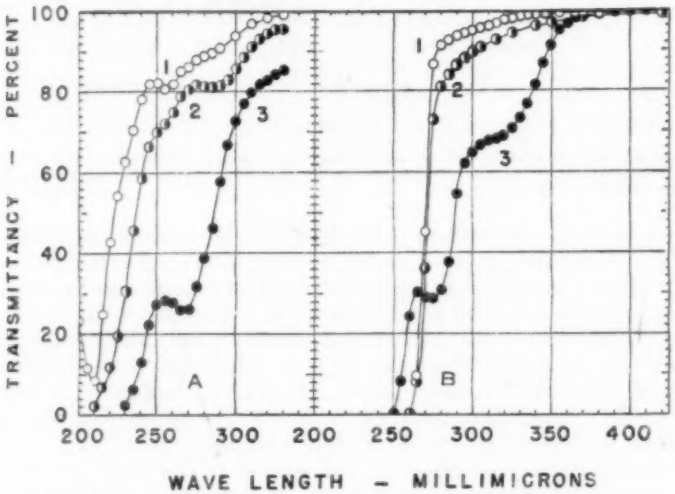

FIGURE 5.—*Ultraviolet-absorption spectra of different specimens.*

A, Commercial methyl alcohol. 1 and 2, samples *X* and *Y*, respectively, both untreated; 3, sample Z, a year after purification.
B, Commercial ethyl acetate. 2 and 3, "absolute" grade, samples *X* and *Y*, respectively; 1, sample *X* after purification.

Ethyl alcohol.—In figure 6, A, curves 2 and 1, respectively, show the absorption of commercial 95-percent ethyl alcohol before and after simple distillation. The spectrum of commercial "absolute" ethyl alcohol showed a double shoulder in the region 250 to 270 mμ, which in part may have been due to a trace of benzene used in the industrial process for dehydrating 95-percent ethyl alcohol.[10]

Ethyl acetate.—Curves 2 and 3 in figure 5, B, represent, respectively, two commercial grades, *X* and *Y*, of "absolute" ethyl acetate from freshly opened bottles. Curve 1 was obtained by washing it with dilute alkali and water, drying, and distilling.

[10] Traces of benzene may be present in various organic solvents [2].

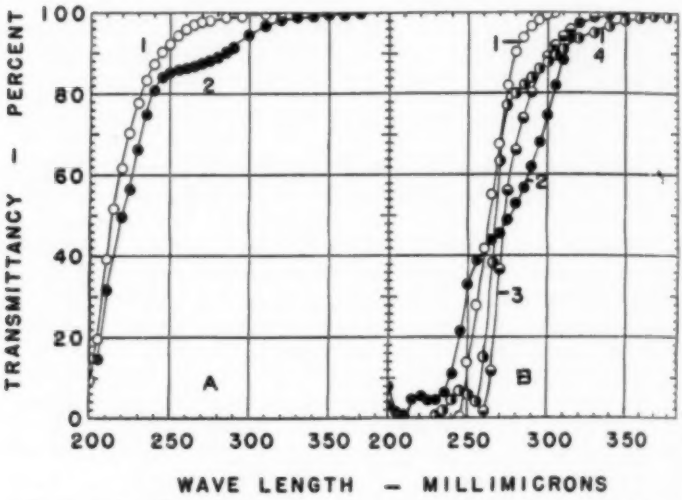

FIGURE 6.—*Ultraviolet-absorption spectra of different specimens.*

A, Commercial 95-percent ethyl alcohol. 1, after distillation; 2, before distillation.
B, Dioxane. 1 and 2, different fractions from purification; 3, purified dioxane after more than a year and a half; 4, commercial dioxane.

Dioxane.—The absorption curves of four specimens of dioxane are presented in figure 6, B. Curve 4 was obtained with commercial dioxane. Curves 1 and 2 represent different fractions from distillation of the same dioxane after prolonged refluxing with an excess of sodium. The curves were obtained immediately after collecting the fractions. The sample that gave curve 1 had the dielectric constant 2.199, and the one that gave curve 2 had the constant 2.213, both at 30° C.[11] The specimen that gave curve 3 was part of the middle fraction of a sample of dioxane that had been purified in a similar way more than a year and a half earlier. Different investigators who have used dioxane as a solvent in the determination of dipole moments have obtained dielectric constants differing by as much as 7.5 percent at 25° C. Examination of the ultraviolet absorption spectra of specimens used for such measurements would probably account for some of the discrepancies and aid in deciding the most acceptable value for the dielectric constant.

Dimethyldioxane of commercial grade gave a very smooth band between 310 and 400 mμ, with the principal cutoff between 315 and 365 mμ.

Acetone.—A commercial high grade of acetone showed greater transmittancy (e. g., 3.5 percent greater at 350 mμ) after it had stood over anhydrous calcium chloride and had been redistilled. Neither sample showed measurable transmission of light up to 325 mμ, and the purified sample showed complete transmittancy above 390 mμ.

[11] Fractionation of these two samples and measurement of the dielectric constants were performed by A. A. Maryott.

5. CARBON BISULFIDE

A commercial-grade carbon bisulfide showed complete transmission of light at 430 mμ but did not show measurable transmission below 375 mμ. A trace of this carbon bisulfide in purified benzene produced an absorption band near 320 mμ (see discussion on p. 276).

6. USE OF ORGANIC SOLVENTS AS SPECTRAL FILTERS

Ordinarily "filter photometry" is carried out by means of filters isolating certain narrow spectral regions. However, it has occasionally proved feasible to obtain spectroradiometric data by the use of "sharp cutoff" filters, such as those illustrated in this paper. Examples of this type of work are the experiments of (1) Koller and Taylor [15], who accomplished this effect in their studies of erythema due to ultraviolet light by using a Corex filter and changing the concentrations of their (Cd and Mg) photosensitive elements, and of (2) Coblentz [16], who in his study of stellar radiometry obtained data on the spectral distribution of stars by use of sharp cutoff glasses. It is possible that some of the organic solvents described in this paper could be used for similar kinds of work in the ultraviolet, especially because narrow-band filters are almost unattainable below 300 mμ. For such purposes the solvents listed in table 1 are suggested.

TABLE 1.—*Possible solvents for use as cutoff filters*

Solvent	Figure number	Region of spectral cutoff
		mμ
2,2,4-Trimethylpentane, best sample	3, A	210 to 230
Carbon tetrachloride, best sample	4, B	260 to 290
Ethyl acetate, best sample	5, B	265 to 275
Cyclohexane, commercial	2, A	270 to 280
Benzene, best sample	4, A	280 to 300
Dimethyldioxane, commercial		315 to 365

The data in table 1 refer to 1-cm layers; longer or shorter layers of solvent could be used as desired.

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VAPOR PRESSURE, LATENT HEAT OF VAPORIZATION, AND TRIPLE-POINT TEMPERATURE OF N_2O

By Harold J. Hoge

ABSTRACT

The vapor pressure of N_2O has been measured from the triple point (T=182.351° K=—90.809°C, p=658.9 mm Hg) to 236°K (p=10.25 atm). The data are compared with previous work in a graph that includes the entire liquid range.

The latent heat of vaporization was measured from the triple point to 205° K. At the boiling point (184.695°K=—88.465°C) the latent heat is 16.55 kj mole^{-1}. The consistency of the data was tested with Clapeyron's equation, which was also used to compute latent heats above the range of the direct measurements.

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I. INTRODUCTION

A survey of the literature on the vapor pressure of N_2O reveals the fact that the agreement between the results of different observers is poor. Much of the work is very old and shows differences of more than 20 percent, whereas among the more recent papers there are insufficient data to establish the vapor-pressure curve with any great degree of accuracy. The situation with regard to latent heats of vaporization is likewise unsatisfactory, as only a single value [1][1] has been reported since 1900.

As the time that could be devoted to this investigation was limited, it was decided to dispense with the use of a piston gage, and to make all pressure measurements above 2 atmospheres with a Bourdon gage. This resulted in a considerable sacrifice of accuracy, but it is thought

[1] Figures in brackets indicate the literature references at the end of this paper.

that in spite of this the data are considerably more accurate than any previously available. Vapor pressures below 2 atmospheres were measured with a mercury manometer, while latent heats of vaporization were obtained with an adiabatic calorimeter.

II. MATERIAL

Commercial N_2O prepared for anaesthetic purposes was slowly admitted to a trap which was essentially an unsilvered Dewar flask. The inner tube of the trap was filled with liquid air. Solid N_2O collected on the outside of this tube, while noncondensible gases were pumped off with a diffusion pump. When about 25 g of N_2O had been collected the valve in the supply line was closed. After the vacuum became good, the line to the vacuum pump was also closed and the trap allowed to warm up. The solid then fell from the tube to the bottom of the trap and melted, and the liquid was distilled into a cylinder cooled with liquid air, where it could be stored for future use. The pressure in the trap was observed on a manometer during distillation and kept near 1 atmosphere by partially closing the valve to the receiving cylinder. The last 5 or 10 percent of the liquid was discarded.

As judged by the narrowness of the melting range, this simple purifying procedure was adequate, and we may conclude that either the starting material was very pure or the impurities it contained were easily removed.

III. VAPOR PRESSURE

Vapor pressures below 2 atmospheres were measured with the N_2O in an adiabatic calorimeter.[2] The filling tube of the calorimeter transmitted the pressure to a mercury manometer which gave either the absolute pressure, or the excess above barometric pressure, as desired. Column heights were reduced to 0 °C in the usual way, and were reduced to standard gravity by multiplying by the factor 980.10/980.665.

All vapor pressures above 2 atm, and a few which overlapped the manometer data, were measured with a 12-inch Bourdon gage. This gage, which had a range of 0 to 11 atm, was calibrated before and after the measurements. The latter calibration was the more thorough, and was made without resetting the zero of the pointer. It was therefore used in reducing the results. Comparison of the original and final calibrations did not show any lack of stability in the gage. All oil was washed from the gage before use.

The bulb that contained the liquid N_2O was a thin-walled monel tube $\frac{5}{16}$ by 20 inches, the lower part of which was immersed in the stirred liquid cryostat described by Scott and Brickwedde [2]. Connections to the gage and to the cylinder of purified N_2O were made with copper tubing (0.1 in. od). Temperatures were measured with platinum resistance thermometer *G*, previously calibrated [3] on the International Temperature Scale. This thermometer was placed in

[2] This calorimeter was first used by Scott, Meyers, Rands, Brickwedde, and Bekkedahl in the measurement of the vapor pressure and other thermodynamic properties of 1,3-butadiene.

the liquid bath beside the bulb containing the liquid N_2O. Data were taken by raising the temperature of the bath to the desired value and reading the gage at intervals until it was apparent that equilibrium had been reached. Usually there was no significant change during this period.

The results of the vapor pressure measurements are given in table 1. The Antoine equation

$$\log_{10}p(\text{atm})=4.1375-\frac{656.60}{T-26} \tag{1}$$

represents the data within the experimental error. In this equation, T is the Kelvin temperature$=273.16+t°$ C. Hence the denominator of the last term may be written in the alternative forms $T-26=t+247.16$. Deviations of the observed pressures from those calculated from this equation are given in table 1. The scattering of the data may be seen in figure 1, where [log p (observed)$-$log p (calculated)] is plotted versus T. Data of other observers are also given in this graph, and are discussed in a later section of this paper.

TABLE 1.—*Observed vapor pressures of* N_2O

[Pressures given to 3 decimal places were measured with a Bourdon gage, while those given to 4 places were measured with a mercury manometer and barometer. Calculated values were obtained from eq 1. Data are given in the order in which they were obtained]

T	p(obs)	Δp(obs.−calc.)
°K	atm	atm
198.41	2.130	−0.004
204.14	2.831	.002
208.71	3.495	−.003
212.18	4.066	−.015
215.18	4.645	.003
218.92	5.417	−.003
222.59	6.269	−.006
226.44	7.275	.002
231.03	8.612	.002
236.86	10.589	.031
197.98	2.092	.005
208.88	3.524	−.001
215.31	4.674	.006
222.41	6.222	−.008
231.48	8.752	.000
236.54	10.464	.019
193.31	1.640	.007
200.61	2.375	−.008
206.95	3.229	.002
210.11	3.726	.000
217.12	5.038	.003
224.04	6.637	.000
230.63	8.499	.011
235.61	10.120	.004
183.313	0.9200	.0002
184.625	.9955	−.0004
186.578	1.1184	.0003
188.425	1.2447	.0002
191.703	1.4966	.0004
194.407	1.7324	.0002
197.048	1.9891	−.0007

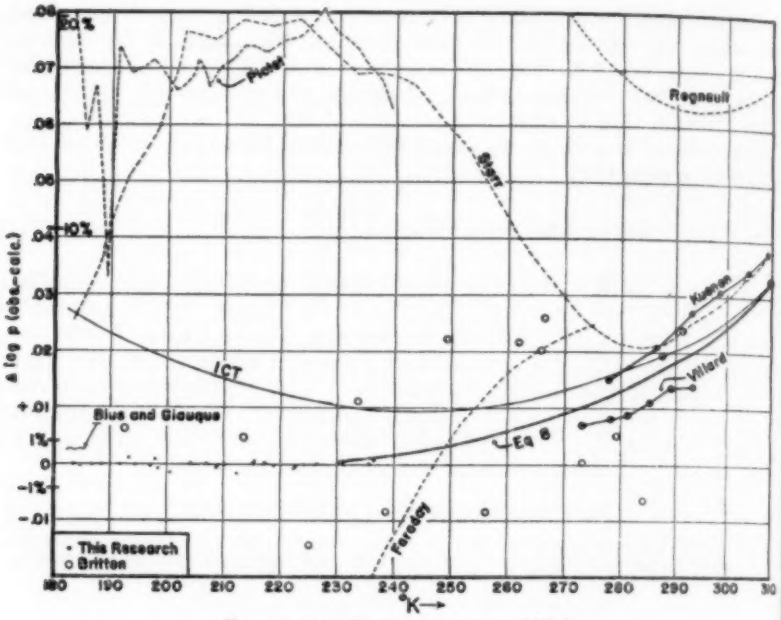

FIGURE 1.—*Vapor pressure of* N_2O.

The ordinates are deviations of observed values from those calculated from the equation $\log_{10} p(\text{atm}) = 4.1375 - \frac{656.60}{T-26}$. This equation represents the data obtained in this research within the experimental error but at higher temperatures it gives pressures that are too low.

Table 2 contains values of p computed from equation 1 at 5-degree temperature intervals. It is hoped that the vapor pressures in this table are correct to 1 percent or better throughout the entire range. Where the mercury manometer was used (below 2 atm) they are of course much better.

TABLE 2.—*Vapor pressures and latent heats of vaporization of liquid* N_2O, *at uniform temperature intervals.*

[Pressures were computed from eq 1, latent heats from eq 5. Molecular weight=44.016.]

T	p	L	L
°K	*atm*	*kj mole*$^{-1}$	*j g*$^{-1}$
[a] 182.351	0.8670	16.66	378.6
[b] 184.695	1.0000	16.55	376.0
185	1.018	16.54	375.7
190	1.361	16.29	370.2
195	1.788	16.04	364.4
200	2.312	15.78	358.4
205	2.946	15.50	352.1
210	3.707	15.21	346
215	4.607	14.91	339
220	5.662	14.59	331
225	6.887	14.26	324
230	8.297	13.91	316
235	9.906	13.54	308
240	11.730	13.15	299

[a] Triple point.
[b] Boiling point.

IV. TRIPLE POINT AND BOILING POINT

To test the purity of the N_2O, and to determine the triple point temperature, a portion of the purified material was placed in the calorimeter and its temperature determined as a function of the fraction melted. The measurements included a determination of the gross heat capacity both above and below the triple point, so that the heat required to melt the sample without raising its temperature could be determined. The value thus obtained was used in computing the fraction melted, but did not lead to a value of the heat of fusion per gram, as no suitable means of measuring the mass of material was available at the time.

Temperature as a function of fraction melted is shown in figure 2, where the two types of circles refer to two different runs on the same sample. The equation of the curve in the figure is

$$182.351 - T = (RT_f^2/L_f)(7.10^{-6}/F), \qquad (2)$$

where T_f is the temperature of fusion, L_f the latent heat of fusion, and F the fraction of the material melted. Assuming this equation to represent the depression of the melting point by impurity, the mole

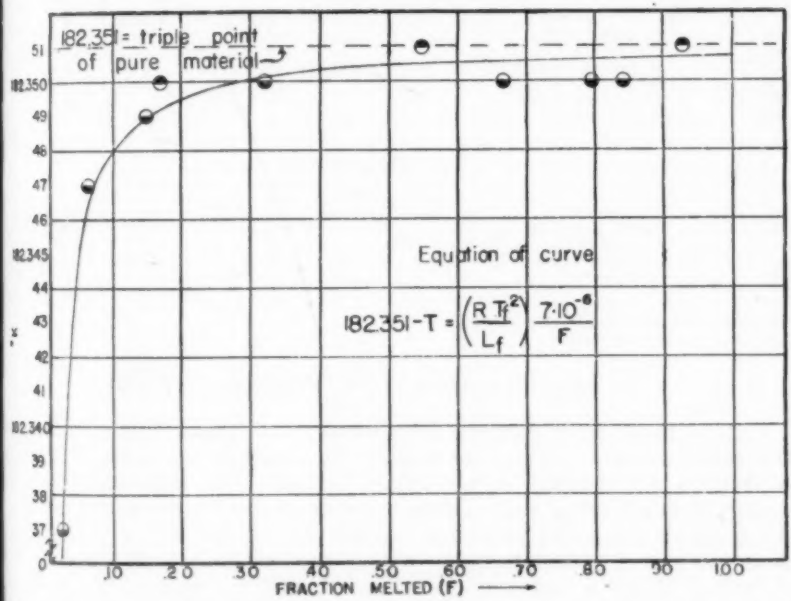

FIGURE 2.—*Temperature of a sample of N_2O as a function of the fraction of the material melted.*

fraction of impurity is 7×10^{-6}, and the melting point of pure N_2O is 182.351°K. Blue and Giauque's [1] value for the latent heat of fusion was used (1563.0 cal mole^{-1}). The triple-point pressure, found by substituting 182.351°K in equation 1 is 0.8670 atm, or 658.9 mm Hg. The boiling point, calculated from the same equation, is 184.695°K. These values are probably correct within ±5 millidegrees on the International Temperature Scale. The temperature measurements

were made with platinum resistance thermometer *B*, which was calibrated in the same way [3] as thermometer *G*, used in the measurement of vapor pressures above 2 atm.

The triple point and boiling point of N_2O give promise of being satisfactory thermometric fixed points at which the calibration of thermometers may be checked. In view of their possible usefulness for this purpose, values of the triple- and boiling-point temperatures reported since 1900 have been assembled in table 3. The triple-point pressure is included where available. A more exhaustive study would be required to establish the reliability of these two fixed points under all conditions likely to arise in practice, but there is as yet no indication that they would be unsatisfactory.

TABLE 3.—*Values of the triple point and boiling point of* N_2O *published since 1900*

[Temperatures are given as reported by the authors, without conversion from centigrade to absolute or vice versa]

Date	Reference	t	T	p	Thermometer
			N_2O, BOILING POINT		
		°C	°K	mm Hg	
1904	Grunmach [21]	−89.4		741.1	Pentane.
1906	Hunter [22]		186.0		[a] Pt resistance.
1916	Burrell and Robertson [23]	−88.7	184.4		Pentane.
1922	Bergstrom [24]	−89.5			[b] Toluene.
1935	Blue and Giauque [1]		184.59		Thermel.
1944	This research		184.695		Pt resistance.
			N_2O, TRIPLE POINT		
1906	Hunter [22]		183.9	660	[a] Pt resistance.
1916	Burrell and Robertson [23]	−90.6	182.5	666	Pentane.
1930	Clusius, Hiller, and Vaughen [25]		182.4		Pb resistance.
1935	Blue and Giauque [1]		182.26	658.96	Thermel.
1944	This research		182.351	658.9	Pt resistance.

[a] Using Callendar equation, no β-term.
[b] 2 thermometers were used.

V. LATENT HEAT OF VAPORIZATION

Latent heats were measured by vaporizing liquid N_2O contained in the calorimeter. Vapor was withdrawn through the filling line, which contained a partially closed valve (outside the calorimeter), while energy was added at such a rate as to keep the temperature constant. At a given time the escaping stream was diverted to a previously weighed monel cylinder cooled with liquid air, in which the N_2O condensed. When a sufficient quantity of material had been vaporized, which generally required from 15 to 30 minutes, the stream was diverted to another receiver. The monel cylinder was then allowed to warm to room temperature and the increase in weight determined. Since the cylinder had to withstand the vapor pressure of N_2O at room temperature (about 55 atm), it was necessarily rather heavy (weight empty 956 g, internal volume 324 cm^3). During the weighings an airtight counterpoise, which displaced approximately the same volume of air as the cylinder, was used to minimize errors due to changes in the buoyant force of the air.

The results are given in table 4. The molar latent heat is given by

$$L=44.016\,(Q/M)\,(1-V_l/V_g), \tag{3}$$

where 44.016 is the molecular weight; and M is the mass of N_2O expelled from the calorimeter by addition of the energy Q. The quantities V_l and V_g are the molar volumes of the liquid and vapor phases under the conditions of the experiment, and the factor $(1-V_l/V_g)$ takes account of the vaporized material that remains in the calorimeter to fill the space formerly occupied by liquid. The correction for vapor remaining in the calorimeter is relatively unimportant in the range covered by the present measurements, as may be seen from the values of $(1-V_l/V_g)$ given in table 4. Values of V_l were taken from reference [4], whereas values of V_g were computed from an equation proposed by Meyers [5], which may be written in the form

$$(1-V_g/V_i)\,(1-V_l/V_i)=(p/ep_c)^{0.7}. \tag{4}$$

In this equation, V_g and V_l are, as above, the molar volumes of saturated vapor and liquid in equilibrium with each other, and V_i is RT/p, the volume which an ideal gas would occupy under the same conditions. Also, p is the vapor pressure and p_c the critical pressure of the substance, taken in this case to be 71.7 atm [6], and e is the base of natural logarithms.

TABLE 4.—*Experimentally determined latent heats of vaporization*

[M is mass of gas expelled from calorimeter by addition of energy Q. From these the molar latent heat L is obtained with the aid of eq 3]

T	p(calc.)	M	Q/M	$(1-V_l/V_g)$	L	ΔL(obs.−calc.)
°K	*atm*	*g*	*j g*$^{-1}$		*kj mole*$^{-1}$	*kj mole*$^{-1}$
185.458	1.047	2.508	377.1	0.9974	16.55	0.03
187.243	1.163	11.854	374.1	.9972	16.42	−.01
188.535	1.253	3.956	371.9	.9970	16.32	−.05
184.369	0.9806	16.949	377.8	.9976	16.59	.02
194.944	1.782	11.402	367.1	.9957	16.09	.05
200.445	2.364	9.449	359.9	.9944	15.75	.00
204.945	2.939	18.793	354.3	.9930	15.48	−.02
193.135	1.618	14.232	367.9	.9961	16.13	−.01
194.666	1.756	12.643	366.7	.9958	16.08	.02
196.419	1.926	12.580	363.8	.9954	15.94	−.03
198.643	2.159	13.289	361.3	.9948	15.82	−.03
185.910	1.075	12.242	375.6	.9974	16.49	.00

The experimental data are represented within the accuracy of the measurements by the equation

$$L(\text{kj mol}^{-1})=1.571(T_c-T)^{0.57}-0.0646(T_c-T), \tag{5}$$

where T_c is the critical temperature, taken to be 309.7°K [6].

Deviations of the observed values from this equation are given in table 4. The experimental points are plotted as circles in figure 3; the solid line corresponds to equation 5. This equation represents

both the experimental values given in table 4 and also values of L at higher temperatures, which were computed from vapor-pressure data with the aid of Clapeyron's equation.

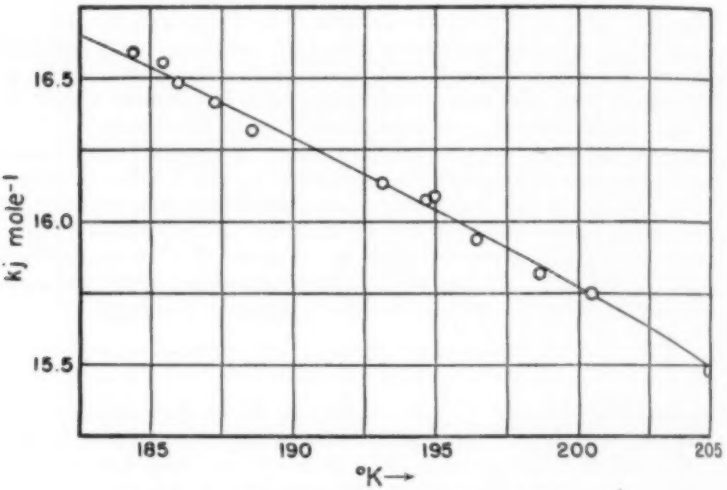

FIGURE 3.—*Heat of vaporization of* N_2O.

VI. COMPUTATIONS OF LATENT HEAT FROM CLAPEYRON'S EQUATION

Clapeyron's equation, written in the form

$$L=T\frac{dp}{dT}(V_g-V_l), \tag{6}$$

was used to compute values of L at 5-degree intervals throughout the entire range of the vapor-pressure measurements, which was approximately 183° to 240° K. Below 205° K the computed values could be compared with the directly observed values of L, and furnished a test of the consistency of the experimental measurements of vapor pressure and latent heat. Above 205° there were no direct observations of L, and equation 6 gave values not otherwise available. Values of dp/dT were obtained from equation 1. The values of V_l were taken from reference [4].

The most uncertain quantity entering into the calculation appeared to be V_g. Two methods were used for obtaining V_g, the first of which was based on work of Johnston and Weimer [7]. These authors used a gas thermometer to measure the second virial coefficient [3] of N_2O. When vapor volumes computed from their data were used in equation 6, values of L were obtained that were about 4 parts per thousand lower than the observed values. Vapor volumes were also

[3] The equation which they give for the second virial coefficient contains a misplaced decimal point. The coefficient of the term in $1/T$ must be multiplied by 10 in order to obtain agreement with the graph. The correction is given in J. Am. Chem. Soc. **57**, 2737 (Dec. 1935).

obtained from equation 4. When these were used, somewhat better agreement was obtained, the values of L. being within about 1 part in a thousand of the observed values.

An equation of the form

$$L=A(T_c-T)^{\alpha}+B(T_c-T) \tag{7}$$

was chosen to represent both the experimental values and those at higher temperatures calculated from equations 1, 4, and 6. Equation 7 gives a suitable temperature dependence of L near the critical temperature, and has been found to give a satisfactory representation of the latent heats of a number of substances. From equation 7 we may readily derive the equation

$$\log [L+(T_c-T)dL/dT]=\log[(1-\alpha)A]+\alpha \log(T_c-T)$$

so that by plotting $\log [L+(T_c-T)dL/dT]$ versus $\log (T_c-T)$, a straight line of slope α should be obtained. Since the direct observations covered too small a range to determine α with any great accuracy, the values of L calculated from equation 6, with vapor volumes from equation 4, were used for this purpose. The derivative dL/dT was computed by the method of Rutledge [8], and the logarithmic plot gave the value 0.57 for α. The constant A could also have been obtained from this graph, but it was thought preferable to determine both A and B from the directly observed values of L. This led to equation 5, which was used to compute the values of L given in table 2. On comparing these with the values of L used in the determination of α, the greatest difference was found to be less than 1 part in a thousand. The agreement is considered to some extent fortuitous.

It is thought that the latent heats of vaporization given in table 2 are within 3 parts in a thousand of the true values in the range when direct determinations were made (up to 205°K). Above 205°K the uncertainty progressively increases, and may approach 2 percent at the highest temperatures.

VII. COMPARISON WITH PREVIOUS WORK

Cragoe [4] has analyzed the data on the vapor pressure of liquid N_2O extant at the time of publication of the International Critical Tables, and derived from them a table of values which is represented by the curve in figure 1 marked ICT. At the lower temperatures this table now appears to give pressures that are too high, primarily because the temperature assigned to the boiling point was too low. At the time of that analysis there were no satisfactory data at intermediate pressures. Since that time measurements have been made by Britton [9] and by Blue and Giauque [1]. Their results are shown in figure 1. Britton's values scatter considerably, but show no systematic deviation from those found in the present research.

Blue and Giauque measured vapor pressures of both solid and liquid, but covered a range of only 3.6 degrees in the liquid. The triple-point pressure reported by them and that found by the author are in excellent agreement, as may be seen from table 3. In view of

this, it may at first appear surprising that on figure 1 their pressures are more than 5 parts in a thousand higher than those of the author. The reason for this is almost certainly a difference in temperature scales. Blue and Giauque give 182.26° K for the triple point. This value was obtained with a thermocouple which they estimate may be in error by several hundredths of a degree, although greater accuracy in the measurement of small temperature intervals was obtained by use of a gold resistance thermometer which was calibrated from time to time by comparison with the thermocouple. The thermocouple was originally calibrated by comparison with a hydrogen gas thermometer. Their triple-point temperature is 0.09 degree lower than that found in the present research, and raising all of their temperatures by this amount removes the small discrepancy between their results and the author's.

Although agreement of temperature scales within 0.09 degree may be considered satisfactory in many applications, it is of interest to consider the possible causes of the discrepancy in the present instance. Part of the discrepancy can be accounted for by the fact that the author's temperatures are based on $T_0=273.16°$ K, whereas Blue and Giauque used $T_0=273.1$. When this difference is taken into account the discrepancy is reduced by a maximum of 0.06 degree. The remaining 0.03 degree must be accounted for by errors in the two scales or by a difference between the International Temperature Scales and the thermodynamic temperature scale. In this temperature region the International Scale is believed to be reproducible to better than 0.01 degree. The remaining discrepancy could conceivably be due to a difference between the International Scale and the thermodynamic, but it is opposite in sign to the values of this difference previously reported [10, 11].

The range covered by figure 1 has been extended from 240° K to the critical point primarily for the benefit of those who may require values of the vapor pressure beyond the range of the present work. The most reliable data in this range appear to be those of Villard [12] and Kuenen [13]. The fact that these data give positive deviations in figure 1 is to be expected, as the Antoine equation is known to give pressures that are too low in the critical region when the constants are determined from data at lower temperatures.

Data from Starr [14], Pictet [15], Regnault [16] and Faraday [17] are also shown in figure 1. None of these sets of data shows the correct temperature dependence, and little or no weight can be given to them. Although Starr's table is in error by almost 20 percent over part of the range, it has found its way into tables of refrigerating data [18] and as recently as 1941 appeared in the Chemical Engineers' Handbook [19]. It is interesting to note that the latter reference also contains (p. 375) the ICT vapor-pressure table, which gives more nearly correct values. It is not clear whether Starr made measurements himself or whether he based his table on earlier work.

The heavy curve in figure 1 extending from 230° K to the critical point was drawn to represent the probable course of the vapor-pressure curve in this region.

This curve represents the vapor-pressure equation

$$\log p = 4.52620 - (1/T)[829.148 + 1.157y\ 10^{-4}(10^{3.4y2\ 10^{-10}} - 1)] \quad (8)$$

where $y = 69{,}500 - T^2$, and $T = 273.16 + t°$ C. The author is indebted to C. H. Meyers for deriving this equation. He has used this form of equation with success for representing the vapor pressures of CO_2 [20] and other substances for which accurate data were available. Equation 8 may be used alternatively with equation 1 in the range covered by the author's data, as the two equations agree within less than the experimental error. Equation 8 would appear to give as reliable values of vapor pressure above 240° K as present data permit, but subsequent measurements may well show these to be substantially in error at the higher pressures.

The critical temperature and pressure given by equation 8 are those accepted by Pickering [6]: $p_c = 71.7$ atm, $t_c = 36.5°$ C, which agree with those given in reference [4].

For the heat of vaporization at 1 atmosphere, Blue and Giauque [1] give 3958 ± 3 cal mole^{-1}. Converting this to international joules, we find $16.55_7 \pm .013$ kj mole^{-1}, which is to be compared with 16.55 kj mole^{-1} found in the present investigation.

VIII. TABLES IN ENGINEERING UNITS

For the convenience of those who prefer to use engineering units, data given in the preceding sections of this paper have been converted with the aid of the following data:

$f(°F) - 32 = 1.8[T(° K) - 273.16]$.
1 atm = 14.696 psi.
1 j g^{-1} = (1.8 × 860)/3600 Btu lb^{-1}
= 0.43000 Btu lb^{-1}.

By substituting these relations into equations 1 and 5, we obtain the alternative forms

$$\log_{10} p(\text{psi abs}) = 5.3047 - \frac{1181.88}{f + 412.89} \quad (1a)$$

and

$$L(\text{Btu lb}^{-1}) = 10.978(f_c - f)^{0.57} - 0.3506(f_c - f), \quad (5a)$$

where f is the temperature in degrees fahrenheit, and f_c, the critical temperature, is 97.8° F. Equations 1a and 5a have been used to compute values of p and L at intervals of 10 degrees fahrenheit between the triple point and −30° F (238.716° K). These are given in table 5. Above −30° F, vapor pressures have been computed with the aid of equation 8. It is emphasized again that the present investigation did not extend above −30° F and that vapor pressures in this region are based on an analysis of previously published work.

TABLE 5.—*Vapor pressures and heats of vaporization of liquid N_2O in engineering units*

Temperature	Pressure	Heat of vaporization
° *F*	*psi(abs)*	*Btu lb*$^{-1}$
[a]−131.456	12.741	162.8
[b]−127.237	14.696	161.7
−130	13.39	162.4
−120	18.60	159.8
−110	25.28	157.1
−100	33.68	154.2
−90	44.10	151.2
−80	56.8	148.0
−70	72.1	144.7
−60	90.3	141.2
−50	111.6	137.5
−40	136.5	133.6
−30	165.2	129.5
−20	199.0	
−10	236.8	
0	279.7	
10	328.0	
20	382.1	
30	442.4	
40	509	
50	583	
60	664	
70	754	
80	853	
90	962	
[c]97.8	1,054	

[a] Triple point.
[b] Boiling point.
[c] Critical point.

IX. REFERENCES

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